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Theory of the simplest substitution reactions

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The dynamic equations describing the elementary substitution reactions are deduced. The expressions obtained are analyzed in the heavy mass limit of reacting particles. The connection between the peculiarities of reaction cross section from one side and the bound states characteristics and the regularities of elastic scattering from another is considered. The expressions obtained are compared with experimental data for the simplest substitution reactions.

I. INTRODUCTION

Modern development of experimental methods allows the direct estimation of a number of microscopic features of the elementary chemical reactions. The greatest amount of information is available for gas phase substitution reactions which can be written in the form

$$R_1+R_2\text{–}R_3\rightarrow R_1\text{–}R_2+R_3. \qquad (1)$$

Here the fragment R_k ($k=1, 2, 3$) can be an atom, radical, or ion. The dashes denote chemical bonds.

The experimental results obtained[1–4] [in particular, a distinct angular anisotropy of a number of effective cross sections and the concentration of the energy, released in the course of reactions, at the inner (vibrational and rotational as well as electronic) degrees of freedom] essentially contradict the well known theory of absolute reaction rates,[5] which fairly recently was considered universal. On account of the inadequacy of this theory for the class of simplest reactions which came to be called direct reactions, attempts were made to carry out a complete dynamic calculation of cross sections. The most complete calculation was performed within the framework of the three-particle problem of classical mechanics using effective interaction potentials. The most advanced studies in this direction have been carried out by Karplus and co-workers.[6] Later on they performed the quantum-mechanical calculations as well, which were based on the DWBA method.[7] Similar calculations can also be found in some other papers.[8–11] In all the papers cited a chemical reaction was treated as the motion of point particles along a given energy surface.

It was shown in the work of Brodsky, Levich, and Tolmachev[12] that a purely classical calculation of reaction cross sections is insufficient and that complex many-particle quantum effects always play an important role. So far only the very first steps have been made in the development of an adequate quantum-mechanical description of chemical reactions. Some attempts to solve this problem without resorting to the simplified model of a single potential surface were made, in particular, in Refs. 12 and 13.

This paper is concerned with further treatment of different aspects of the problem stated and especially with finding an adequate theoretical model. We have restricted ourselves to consideration of direct reactions only and assume that no resonances or steady states of the type R_1–R_2–R_3 are formed.

In describing a chemical reaction, it is necessary first of all to take into account the smallness of the electron mass/atomic mass ratio and exploit the possibility of the WKB description of atomic–molecular elastic scattering. For this purpose we use a general approach, similar to some extent to that employed in nuclear reactions theory.[14] The applicability of this approach to the problem under consideration has been considered in our works.[15] The calculation is performed in the center-of-mass system with use of the partial wave expansions, which enables us to take explicitly into account the angular momentum conservation law. We think that in earlier calculations, the law of conservation of angular momentum was not properly taken into account. At the same time, owing to the multiplicity of the approximations used, the violations of invariance with respect to the Galilean group, even if small, can lead to large errors in the final expressions.

In Sec. II the statement of the problem within the framework of the chosen model is considered. Section III gives the general properties of the expression for the reaction cross section. In Sec. IV a calculation for model potentials is carried out. Sections V and VI treat and compare with experiment the basic qualitative and the simplest quantitative consequences of the formulas deduced earlier. In the Conclusions the physical justification of the chosen model and the results obtained are discussed.

II. EXPRESSION FOR THE DIFFERENTIAL REACTION CROSS SECTION

First of all, in the chosen model the real complex quantum system consisting of nuclei and electrons is substituted by a much simpler system composed only of three particles 1, 2, 3 with coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ and masses m_1, m_2, m_3. At the same time, it is assumed, however, that the system under consideration can be in two kinds of states, and accordingly the complete wavefunction can be represented as a sum of two wavefunctions $\Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and $\Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. The wavefunctions Ψ_1 and Ψ_2 differ in that the former at large distances shows nondissappearing asymptotes only in the initial reaction channel (corresponding to the bound states R_1–R_3 and to R_2 tending to infinity) and the latter shows nondisappearing asymptotes only in the final reaction channel (corresponding to the bound states R_1–R_2 and to R_3 tending to infinity). Such an introduction of two functions, accounts for the existence of two different electronic states. Two potential energy functions (to be characterized below) $U_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and $U_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ are also introduced, which account for the difference in the effective interaction between particles in the cases when they form part of initial or final molecules, respectively. Besides the potential energy functions, in what follows the function $V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ will be introduced, which determines the transition from one state to another. Let us introduce two sets of Jacobi coordinates suitable for description of the initial and final states, respectively $(\mathbf{r}_i, \mathbf{R}_i)$, $(\mathbf{r}_f, \mathbf{R}_f)$, where

$$\begin{aligned}
\mathbf{r}_i &= (\mathbf{r}_1-\mathbf{r}_3)[m_1m_3/(m_1+m_3)]^{1/2},\\
\mathbf{R}_i &= [\mathbf{r}_2-(m_1\mathbf{r}_1+m_3\mathbf{r}_3)/(m_1+m_3)][m_2(m_1+m_3)/M]^{1/2},\\
\mathbf{r}_f &= (\mathbf{r}_2-\mathbf{r}_1)[m_1m_2/(m_1+m_2)]^{1/2},\\
\mathbf{R}_f &= [(m_1\mathbf{r}_1+m_2\mathbf{r}_2)/(m_1+m_2)-\mathbf{r}_3][m_3(m_1+m_2)/M]^{1/2};\\
M &= m_1+m_2+m_3.
\end{aligned} \tag{2}$$

Here $\mathbf{R}_i$ is, within the accuracy of the scale factor, the radius vector of particle 2 reckoned from the center of mass of the bound state (1, 3); $\mathbf{r}_i$ is, within the accuracy of the scale factor, the relative distance between 1 and 3. The coordinates $(\mathbf{R}_f, \mathbf{r}_f)$ have a similar meaning with transposition of the indices 1, 2, 3. All further treatment will be confined to the center-of-mass system. In the variables in Eq. (2) the operator of the total kinetic energy will be of the form

$$\begin{aligned}
\mathcal{K} &= -\tfrac{1}{2}\hbar^2(\partial^2/\partial\mathbf{R}_i^2)-\tfrac{1}{2}\hbar^2(\partial^2/\partial\mathbf{r}_i^2)\\
&= -\tfrac{1}{2}\hbar^2(\partial^2/\partial\mathbf{R}_f^2)-\tfrac{1}{2}\hbar^2(\partial^2/\partial\mathbf{r}_f^2).
\end{aligned} \tag{3}$$

Each pair of the coordinates $(\mathbf{r}_i, \mathbf{R}_i)$, $(\mathbf{r}_f, \mathbf{R}_f)$ can be expressed in terms of the other pair using the relations

$$\begin{aligned}
\mathbf{R}_i &= \mathbf{r}_f \sin\eta+\mathbf{R}_f \cos\eta,\\
\mathbf{r}_i &= -\mathbf{r}_f \cos\eta+\mathbf{R}_f \sin\eta;\\
\mathbf{r}_i &= (1/\sin\eta)(\mathbf{R}_f-\mathbf{R}_i \cos\eta),\\
\mathbf{r}_f &= (1/\sin\eta)(-\mathbf{R}_f \cos\eta+\mathbf{R}_i);\\
\mathbf{R}_i &= (1/\sin\eta)(\mathbf{r}_i \cos\eta+\mathbf{r}_f),\\
\mathbf{R}_f &= (1/\sin\eta)(\mathbf{r}_i+\mathbf{r}_f \cos\eta).
\end{aligned} \tag{4}$$

In (4) the angle η has been introduced, which lies in the first quadrant and is determined by a kinematic relation—the rotation from the coordinates $(\mathbf{r}_i, \mathbf{R}_i)$ to the coordinates $(\mathbf{r}_f, \mathbf{R}_f)$:

$$\tan\eta = (Mm_1/m_2m_3)^{1/2}. \tag{5}$$

We shall take the potential energies U_1 and U_2 as the following sums:

$$U_1 = U_i(r_i)+W_i(R_i), \qquad U_2 = U_f(r_f)+W_f(R_f). \tag{6}$$

The potentials $U_\alpha(r_\alpha)$, where $\alpha=i,f$ are chosen such as to ensure formation of bound states. Everywhere, where no special reservations are made, it is assumed that $U_\alpha(r_\alpha)\rightarrow\infty$ at $r_\alpha\rightarrow\infty$. Therefore, the bound state spectrum will be strictly discrete. The potentials $W_\alpha(R_\alpha)$, describing the elastic scattering in the initial and final channels, respectively, are assumed to approach zero quickly enough at $R_\alpha\rightarrow\infty$,

$$W_\alpha(R_\alpha)\rightarrow 0 \quad \text{at} \quad R_\alpha\rightarrow\infty \qquad (\alpha=i,f). \tag{7}$$

The choice of (6) satisfies the necessary condition that the potentials W_α should not cause transitions from channel to channel and makes it possible subsequently to separate the angular variables fairly easily. It is significant that $U_\alpha(r_\alpha)$ and $W_\alpha(R_\alpha)$ can be found from independent measurements of bound states and elastic scattering.

In the absence of interaction between the channels,

$$\begin{aligned}
\Psi_1 &= \Psi_i(\mathbf{R}_i, \mathbf{r}_i) \qquad \text{at } \hat{V}=0,\\
\Psi_2 &= \Psi_f(\mathbf{R}_f, \mathbf{r}_f) \qquad \text{at } \hat{V}\equiv 0.
\end{aligned} \tag{8}$$

The functions Ψ_α being considered $(\alpha=i,f)$, which are solutions of independent Schrödinger equations with the potentials (6), can be written as

$$\Psi_\alpha = \Phi_\alpha(R_\alpha)[\varphi_{n\alpha}(r_\alpha)/r_\alpha]Y_{l\alpha m\alpha}(\hat{\mathbf{r}}_\alpha). \tag{9}$$

Here $Y_{l\alpha m\alpha}(\hat{\mathbf{r}}_\alpha)$ is the normalized spherical harmonic[16] of the angular variables characterizing the vector $\hat{\mathbf{r}}_\alpha = \mathbf{r}_\alpha/r_\alpha$; $\varphi_{n\alpha}(r_\alpha)$ are the real bound state functions satisfying the equations

$$\begin{aligned}
(\tfrac{1}{2}\hbar^2\{(\partial^2/\partial r_\alpha^2)-[l_\alpha(l_\alpha+1)/r_\alpha^2]\}&\\
-U_\alpha(r_\alpha)+\mathcal{E}_{n\alpha})\varphi_{n\alpha}(r_\alpha) &= 0.
\end{aligned} \tag{10}$$

The $\varphi_{n\alpha}(r_\alpha)$ functions are normalized to the δ function of r_α:

$$\sum_{n\alpha}\varphi_{n\alpha}(r_\alpha)\varphi_{n\alpha}(r_\alpha')=\delta(r_\alpha-r_\alpha');$$

the summation sign includes summation over all independent quantum numbers n_α. The functions $\Phi_\alpha(R_\alpha)$ obey the equations

$$[\tfrac{1}{2}\hbar^2(\partial^2/\partial\mathbf{R}_\alpha^2)-W_\alpha(R_\alpha)+\tfrac{1}{2}k_\alpha^2]\Phi_\alpha(\mathbf{R}_\alpha)=0. \tag{11}$$

The total energy of the system E is

$$E=\tfrac{1}{2}k_i^2+\mathcal{E}_{n_i}=\tfrac{1}{2}k_f^2+\mathcal{E}_{n_f}. \tag{12}$$

Later on we shall require the solutions of (11) corresponding to a definite value of the angular momentum and its projections:

$$\Phi_{L_\alpha}{}^{\pm}(\mathbf{R}_\alpha)=R_\alpha{}^{-1}\chi_{L\alpha}{}^{\pm}(R_\alpha)\,Y_{L\alpha M\alpha}(\hat{\mathbf{R}}_\alpha). \qquad (13)$$

Here the solutions $\chi^{\pm}(R_\alpha)$ of the radial equation obtained from (11) are fixed by asymptotic conditions used in the potential scattering theory[17]:

$$\chi_{L\alpha}{}^{\pm}(R_\alpha)\sim(\hbar/k_\alpha)^{1/2}\exp\{\pm i[(k_\alpha/\hbar)R_\alpha-\tfrac{1}{2}\pi(L_\alpha+1)]\}$$
$$\text{at}\quad R_\alpha\rightarrow\infty. \qquad (14)$$

In particular, the wavefunction $\Phi_{k\alpha}(\mathbf{R}_\alpha)$, $\alpha=i, f$, corresponding to the incident plane wave $\exp[(i/\hbar)\mathbf{k}_\alpha\mathbf{R}_\alpha]$ can be written, using the introduced symbols, as

$$\Phi_{k\alpha}(\mathbf{R}_\alpha)=\sum_{L\alpha,M\alpha}\{2\pi i^{L\alpha}(\hbar/k_\alpha)^{1/2}$$
$$\times(1/R_\alpha)\,Y_{L\alpha M\alpha}{}^{*}(\hat{k}_\alpha)\,Y_{L\alpha M\alpha}(\hat{\mathbf{R}}_\alpha)$$
$$\times[\exp(2i\delta_{L\alpha})\chi_{L\alpha}{}^{+}(R_\alpha)+\chi_{L\alpha}{}^{-}(R_\alpha)]\}, \qquad (15)$$

where $\delta_{L\alpha}$ is the scattering phase determined from the regularity condition at $R_\alpha=0$ and is independent of M_α. The complete wavefunction Ψ_i of the channel i corresponding (in the absence of interaction between channels) to (a) the presence of an incident plane wave $\exp[(i/\pi)\mathbf{k}_i\mathbf{R}_i]$ with the relative motion momentum $\mathbf{k}_i[M/M_2(m_1+m_3)]^{1/2}$ and (b) to a definite bound state r_i, can be represented now as

$$\Psi_i(\mathbf{R}_i,\mathbf{r}_i)=\Phi_{k_i}(\mathbf{R}_i)[\varphi_{n_i}(r_i)/r_i]Y_{l_im_i}(\hat{\mathbf{r}}_i). \qquad (16)$$

When the interaction between the channels is introduced in the channel f the wavefunction Ψ_2 arises, which is of the form

$$\Psi_2(\mathbf{R}_f,\mathbf{r}_f)=\int d^3R_i'd^3r_i'\mathcal{G}_f(\mathbf{R}_f,\mathbf{r}_f;\mathbf{R}_f',\mathbf{r}_f')$$
$$\times(\hat{V}\Psi_i)(\mathbf{R}_i',\mathbf{r}_i'), \qquad (17)$$

where $\mathbf{R}_{i1}'\mathbf{r}_i'$, $\mathbf{R}_{f1}'\mathbf{r}_f'$ are related by formulas (4), and $d^3R_idr_i{}^3=d^3R_fd^3r_f$. In writing (17) we introduced, firstly, Green's function for the Schrödinger equation in the final reaction channel corresponding to the final kinetic energy of relative motion $\frac{1}{2}k_f{}^2=E-\mathcal{E}_{n_f}$ of the form[15,17]:

$$\mathcal{G}_f(\mathbf{R}_f,\mathbf{r}_f;R_f',r_f')=-\frac{i}{\hbar^2}\sum_{L_fM_fl_fm_fn_f}\Bigg\{\frac{\varphi_{n_f}(r_f)}{r_fR_f}\,Y_{L_fM_f}(\hat{\mathbf{R}}_f)\,Y_{l_fm_f}(\hat{\mathbf{r}}_f)\{\theta(R_f-R_f')[\exp(2i\delta_{lf})\chi_{L_f}{}^{+}(R_f')$$
$$+\chi_{L_f}{}^{-}(R_f')]\chi_{L_f}{}^{+}(R_f)+\theta(R_f'-R_f)[\exp(2i\delta_{L_f})\chi_{L_f}{}^{+}(R_f)+\chi_{L_f}{}^{-}(R_f)]\chi^{+}(R_f')\}$$
$$\times Y_{L_fM_f}(\hat{\mathbf{R}}_f')\,Y_{l_fm_f}(\hat{\mathbf{r}}_f')\,\frac{\varphi_{n_f}(r_f')}{r_f'R_f'}\Bigg\}. \qquad (18)$$

The summation in (18) is made over all possible values of the angular momenta and their projections L_f, l_f, M_f, m_f and also over the quantum numbers n_f. Secondly, in (17) the basic quantity—the transition operator $\hat{V}$—has been introduced, which can be expressed, at least in principle, in terms of interactions and Green's functions by means of an infinite series. In the heavy particle limit it should be expected that this operator can be approximately reduced to the operator of multiplication by the function $\mathcal{V}(r_i, r_f)$:

$$(\hat{V}\Psi_i)(\mathbf{R}_i,\mathbf{r}_i)\approx\mathcal{V}(r_i,r_f)\Psi_i(\mathbf{R}_i,\mathbf{r}_i).$$

Under sufficiently general assumptions, the function $\mathcal{V}(r_i, r_f)$ is of the form

$$\mathcal{V}(r_i,r_f)=\int_{\rho i0}^{\infty}d\rho_i\int_{\rho f0}^{\infty}d\rho_f\{\tilde{V}(\rho_i,\rho_f)\exp[-(\rho_ir_i+\rho_fr_f)]\},$$

where $\tilde{V}(\rho_i, \rho_f)$ decreases with increasing ρ_α $(\alpha=i, f)$ rapidly enough so that

$$\int_{\rho i0}^{\infty}d\rho_i\int_{\rho f0}^{\infty}d\rho_f\tilde{V}(\rho_i,\rho_f)<\infty.$$

Here the limits $\rho_{\alpha0}$ are determined by the electron binding energies $\mathcal{E}_{\mathrm{el},\alpha}$ as follows:

$$\rho_{\alpha0}\approx(|\,\mathcal{E}_{\mathrm{el},\alpha}\,|\,m_{\mathrm{el}}/\hbar M)^{1/2},$$

i.e., $M^{1/2}/\rho_{\alpha0}$ is much larger than the characteristic dimensions of the problem. This conclusion follows from the essentially quantum nature of electronic motion, allowing tunnel transitions to relatively large distances of the order of 10 Å. For simplicity, below we shall take

$$\mathcal{V}(r_i,r_f)=\mathcal{V}_0\exp[-(\rho_i(r_i+\rho_fr_f)]. \qquad (19)$$

Taking into account that $\Psi_i(\mathbf{R}_i, \mathbf{r}_i)$ tends to zero at $R_f \to \infty$, from (17) by means of (18) and (19) we obtain

$$\Psi_2(R_f, r_f) \underset{R_f \to \infty}{=} -\left(\frac{\hbar}{k_f}\right)^{1/2} \frac{2\pi}{\hbar^2 R_f} \exp(ik_f R_f/\hbar) \sum_{L_f M_f l_f m_f} \left\{ i^{-L_f} Y_{L_f M_f}(\hat{\mathbf{R}}_f) Y_{l_f m_f}(\hat{\mathbf{r}}_f) \frac{\varphi_{n_f}(r_f)}{r_f} \int \frac{d^3R_i' d^3r_i'}{R_f' r_f'} \right.$$
$$\left. \times \left[(\exp(2i\delta_{L_f}) \chi_{L_f}^{+}(R_f') + \chi_{L_f}^{-}(R_f')) Y_{L_f M_f}^{*}(\hat{\mathbf{R}}_f') Y_{l_f m_f}^{*}(\hat{\mathbf{r}}_f') \varphi_f(r_f') \mathcal{V}(r_i', r_f') \Psi_i(R_i', r_i') \right] \right\}. \quad (20)$$

From Expression (20) we obtain the differential cross section of the reaction

$$\boldsymbol{\sigma}(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i) = (k_f/k_i) [M/m_2(m_1+m_3)] \sum_L P_L(\cos\theta) \boldsymbol{\sigma}(L; l_f, m_f, n_f; k_i, l_i, m_i, n_i)$$
$$= (k_f/k_i) [M/m_2(m_1+m_3)] \mid T(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i) \mid^2. \quad (21)$$

Starting from Formula (20) we have used the system of coordinates with the third axis directed along k_i. In view of the fact that in the case under consideration the cross section depends only on the orbital angle θ, we can confine ourselves to consideration of the case of the zero azimuthal angle:

$$\hat{\mathbf{R}}_f = (\theta, 0).$$

It follows from (20) and (21) that

$$T(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i) = -\pi^2 \sum_{L_f L_i} [(2L_i + 1/4\pi)^{1/2} i^{L_i - L_f} Y_{L_f, m_i - m_f}(\theta, 0)] T(L_f, l_f, m_f, n_f; k_i, L_i, l_i, m_i, n_i);$$
$$\boldsymbol{\sigma}(L; l_f, m_f, n_f; k_i, l_i, m_i, n_i) = \pi^3 \sum_{L_f L_i L_f' L_i'} \{ i^{L_i - L_i' - L_f + L_f'} C(L_f, L_f', L; 0, 0) C(L_f, L_f', L; m_i - m_f, m_i - m_f)$$
$$\times [(2L_i+1)(2L_i'+1)(2L_f+1)(2L_f'+1)/4\pi(2L+1)]^{1/2} \mid T(L_f, l_f, m_f, n_f; k_i, L_i, l_i, m_i, n_i) \mid^2 \}. \quad (22)$$

The expression for the quantity introduced $T(L_f, l_f, m_f, n_f; k_i, L_i, l_i, m_i, n_i)$, in accordance with (20) and taking into account (14), (15), (16), and (19) can be written as

$$T(L_f, l_f, m_f, n_f; L_i, l_i, m_i, n_i) = \frac{2\mathcal{V}_0}{\hbar (k_f k_i)^{1/2}} \int \frac{d^3R_i d^3r_i}{R_f R_i r_f r_i}$$
$$\times (Y_{L_f, m_i - m_f}^{*}(\hat{\mathbf{R}}_f) Y_{l_f m_f}^{*}(\hat{\mathbf{r}}_f) \varphi_{n_f}(r_f) \{ [\exp(2i\delta_{L_f}) - 1] \chi_{L_f}^{+}(R_f) + [\chi_{L_f}^{+}(R_f) + \chi_{L_f}^{-}(R_f)] \}$$
$$\times \exp[-(\rho_i r_i + \rho_f r_f)] \{ [\exp(2i\delta_{L_i}) - 1] \chi_{L_i}^{+}(R_i) + [\chi_{L_i}^{+}(R_i) + \chi_{L_i}^{-}(R_i)] \} \varphi_{n_i}(r_i) Y_{L_i 0}(\hat{\mathbf{R}}_i) Y_{l_i m_i}(\hat{\mathbf{r}}_i)). \quad (23)$$

The now superfluous primes on the variables r_α, R_α have been omitted.

In writing (22) and (23), we used the symbols $C(L_f, L_f', L; m, m')$ for the Klebsch–Gordon coefficients from Ref. 16, the formulas for addition of spherical harmonics, and the expression $Y_{L_i M_i}(0, 0) = \delta_{0 M_i} [(2L_i + 1)/4\pi]^{1/2}$. We took into account at once the conservation of the total angular momentum projection. At the same time, the parity conservation law follows directly from the form (23) for nonzero matrix elements (23):

$$(-1)^{L_i + l_i - L_f - l_f} = 1.$$

In the particular case of the vanishing potentials $W_\alpha(R_\alpha) = 0$ the above formulas are significantly simplified. In this case,

$$\delta_{L\alpha} = \delta_{L\alpha}^{0} \equiv 0,$$
$$\chi_{L\alpha}^{+}(R_\alpha) = \chi_{L\alpha}^{0+}(R_\alpha) \equiv (\pi R_\alpha/2)^{1/2} \mathcal{H}_{L\alpha+1/2}^{(1)}(k_\alpha R_\alpha/\hbar),$$
$$\chi_{L\alpha}^{-}(R_\alpha) = \chi_{L\alpha}^{0-}(R_\alpha) \equiv (\pi R_\alpha/2)^{1/2} \mathcal{H}_{L\alpha+1/2}^{(2)}(k_\alpha R_\alpha/\hbar). \quad (24)$$

Here $\mathcal{H}_{L\alpha+1/2}^{(1,2)}$ are the Hankel functions, the half-sum of which is equal to $J_{L\alpha+1/2}(k_\alpha R_\alpha/\hbar)$. Substituting Expressions (24) into Formulas (22) and (23), we have

$$T(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i) \mid_{W_\alpha = 0} = T^0(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i)$$
$$= -\mathcal{V}_0 \int d^3R_i d^3r_i \left[\exp\left(-i \frac{\mathbf{k}_f \mathbf{R}_f}{\hbar}\right) \frac{\varphi_{n_f}(r_f)}{r_f} Y_{l_f m_f}^{*}(\hat{\mathbf{r}}_f) \exp[-(\rho_i r_i + \rho_f r_f)] \right.$$
$$\left. \times \exp\left(i \frac{\mathbf{k}_i \mathbf{R}_i}{\hbar}\right) \frac{\varphi_{n_i}(r_i)}{r_i} Y_{l_i m_i}(\hat{\mathbf{r}}_i) \right]. \quad (25)$$

Here we have introduced the vector $\mathbf{k}_f$ equal in modulus to $k_f = [(E - \mathcal{E}_f) q]^{1/2}$ with the direction $(\theta, 0)$. We have also used the well known Rayleigh formula:

$$\exp[i(\mathbf{k}\mathbf{R}/\hbar)]=\sum_{LM}4\pi i^{L}Y_{LM}^{*}(\hat{\mathbf{k}})\,Y_{LM}(\hat{\mathbf{R}})\,(\pi\hbar/2kR)^{1/2}J_{L+1/2}(kR/\hbar). \tag{26}$$

We shall analyze Expression (23) in subsequent sections. Here we would like to say that some generalizations of U_α, W_α, V would not present any fundamental difficulties. In particular, similar results are obtained if (a) we choose the noncentral expressions for the functions U_α, W_α, V in the form of a finite sum of spherical harmonics of the angles between $\mathbf{r}_\alpha$ and $\mathbf{R}_\alpha$; (b) we include in the expressions for U_α, W_α and V such operators as, e.g., the operators of differentiation with respect to the heavy particle coordinates or transposition operators; (c) we increase the number of the discrete electronic states. We shall not, however, make such generalizations inasmuch as we wish to obtain primarily the results that are slightly dependent on the detailed nature of interactions. It should be emphasized that of the approximations used here, the most advanced (and requiring further analysis) is the disregard for the continuous spectrum contribution of electronic states.

III. GENERAL ANALYSIS OF THE EXPRESSION FOR THE REACTION AMPLITUDE

First of all it is necessary to carry out in the expression for the reaction amplitude (23) that part of the integration over angles which can be done without concretization of the wavefunctions. For this purpose let us accomplish under the integral (23) the rotation in such a way that the third axis should be directed along R_i. Simultaneously let us perform by means of (4) the transition to symmetric variables R_i, R_f. Then we find

$$\begin{aligned}T(L_f,l_f,m_f,n_f;k_i,L_i,l_i,m_i,n_i)={}&\frac{2\mathcal{V}_0}{\hbar(k_ik_f)^{1/2}}\int_0^\infty R_f dR_f\int_0^\infty R_i dR_i\int_0^{2\pi}d\alpha'\int_{-1}^{1}d\cos\beta'\int_0^{2\pi}d\alpha\int_{-1}^{1}d\cos\beta\\&\times\sum_{J_iM_iJ_fM_f\mu_i\mu_f}\{C(L_f,l_f,J_f;m_i-m_f,m_f)C(L_f,l_f,J_f;\mu_f,M_f-\mu_f)C(L_i,l_i,J_i;0,m_i)\\&\times C(L_i,l_i,J_i;\mu_i,M_i-\mu_i)[\varphi_{n_i}(r_i)\varphi_{n_f}(r_f)/r_ir_f]\mathfrak{D}_{M_im_i}^{J_i*}(\alpha',\beta',0)\\&\times\mathfrak{D}_{M_fm_f}^{J_f}(\alpha',\beta',0)\,Y_{L_f\mu_f}^{*}(\beta,\alpha)\,Y_{l_fM_f-\mu_f}^{*}(\gamma_f,\alpha)\,Y_{l_i,M_i-\mu_i}(\gamma_i,\alpha)\,Y_{L_i\mu_i}(0,0)\\&\times[\exp(2i\delta_{L_f})\chi_{L_f}^{+}(R_f)+\chi_{L_f}^{-}(R_f)][\exp(2i\delta_{L_i})\chi_{L_i}^{+}(R_i)+\chi_{L_i}^{-}(R_i)]\}.\end{aligned} \tag{27}$$

In writing (27) we made use of the orthogonality condition for the Klebsch–Gordon coefficients

$$\sum_{j_3}C(j_1,j_2,j_3;m_1,m-m_1)C(j_1,j_2,j_3;m_1',m'-m_1')=\delta_{m,m_1'}\delta_{m,m'} \tag{28}$$

and of the laws of addition and rotation of spherical harmonics with the use of the rotation matrices $D_{MM'}^{J}$ (see Ref. 16). The quantities r_α, γ_α contained in (27) are expressed in terms of the integration variables R_α, β by means of the following relations:

$$\begin{aligned}&r_i=(1/\sin\eta)\,|R_fe^{i\beta}-R_i\cos\eta|, &&r_f=(1/\sin\eta)\,|-R_f(\cos\eta)e^{i\beta}+R_i|,\\&\exp(i\gamma_i)=[(R_fe^{i\beta}-R_i\cos\eta)/(R_fe^{-i\beta}-R_i\cos\eta)]^{1/2}, &&\exp(i\gamma_f)=[(-R_fe^{-i\beta}\cos\eta+R_i)/(-R_fe^{i\beta}\cos\eta+R_i)]^{1/2}.\end{aligned} \tag{29}$$

The cuts on the complex plane β at the square roots in ($2g$) are chosen so that γ_α should change in the range 0–π. In particular, the following equalities are valid:

$$\begin{aligned}&\gamma_i=0 \text{ at} &&\beta=0 \text{ and } R_f>R_i\cos\eta;\\&\gamma_i=\pi \text{ at (I)} &&\beta=0 \text{ and } R_f\leq R_i\cos\eta, \text{ (II) } \beta=\pi;\\&\gamma_f=0 \text{ at (I)} &&\beta=0 \text{ and } R_f\cos\eta\leq R_i, \text{ (II) } \beta=\pi;\\&\gamma_f=\pi \text{ at} &&\beta=0 \text{ and } R_f\cos\eta>R_i.\end{aligned} \tag{30}$$

The cosine of the angle δ between r_i and r_f is defined by the equation:

$$\cos\delta=\cos(\gamma_i-\gamma_f). \tag{31}$$

The angle δ vanishes when the conditions $\beta=0$ and $R_i\geq R_f\cos\eta\geq R_i\cos^2\eta$ are both satisfied. Using the formula

$$\int_0^{2\pi}d\alpha\int_{-1}^{1}d\cos\beta\{\mathfrak{D}_{m_1m}^{l_1*}(\alpha,\beta,0)\mathfrak{D}_{m_2m}^{l_2}(\alpha,\beta,0)\}=\frac{4\pi}{2l_1+1}\delta_{l_1l_2}\delta_{m_1m_2}$$

and the expression for $Y_{LM}(0,0)$ mentioned, we obtain

$$\begin{aligned} T(L_fl_fm_fn_f;\, k_iL_il_im_in_i) = {} & \frac{2V_0}{\hbar\sin^3\eta[(k_ik_f)^{1/2}]}\sum_{JM\mu}\left\{\frac{8\pi^2}{2J+1}\left(\frac{2L_i+1}{4\pi}\right)^{1/2}\right. \\ & \times C(L_fl_fJ;\, m_i-m_f,\, m_f)C(L_il_iJ;\, 0,\, m_i)C(L_il_iJ;\, 0M)C(L_fl_fJ;\, \mu,\, M-\mu) \\ & \times\int_0^\infty R_fdR_f\int_0^\infty R_idR_i\int_{-1}^1\frac{d\cos\beta}{r_ir_f}\{Y_{L_f\mu}{}^*(\beta,0)Y_{l_fM-\mu}{}^*(\gamma_f,0)Y_{l_iM}(\gamma_i,0) \\ & \times\varphi_{n_f}(r_f)\varphi_{n_i}(r_i)[\exp(2i\delta_{L_f})\chi_{L_f}{}^+(R_f)+\chi_{L_f}{}^-(R_f)]\exp[-(\rho_ir_i+\rho_fr_f)] \\ & \left.\times[\exp(2i\delta_{L_i})\chi_{L_i}{}^+(R_i)+\chi_{L_i}{}^-(R_i)]\}\right\}. \qquad (32) \end{aligned}$$

The expression (32) in which an explicit form of total momentum and angular momentum conservation laws are taken into account can be used as a basis for approximate calculations of the reaction cross section. In particular, we can substitute in this expression the one-dimensional radial WKB wavefunctions. Let us consider the problem of optimum choice of the wavefunctions mentioned in the r_α, R_α value range adding the main contribution to the integrals (32). Using the conventional method of analysis of the solutions of the Schrödinger equation, we shall write the functions $\varphi_{n\alpha}(r_\alpha)$ as

$$\varphi_\alpha(r_\alpha)=\Pi_{n\alpha}(r_\alpha)\exp[-(1/\hbar)f_\alpha(r_\alpha)],\qquad \alpha=i,f. \qquad (33)$$

Here $f_\alpha(r_\alpha)$ is the real function turning to ∞ at $r_\alpha\rightarrow\infty$ and $\Pi_{n\alpha}(r_\alpha)$ is the polynomial of r_α. Let $r_{\alpha0}$ be a root of the equation

$$df_\alpha(r_\alpha)/dr_\alpha=0. \qquad (34)$$

If the potentials $U_\alpha(r_\alpha)$ have only one minimum, by the choice of the polynomial $\Pi_\alpha(r_\alpha)$ we can attain the uniqueness of the root (corresponding to the minimum $f_\alpha(r_\alpha)$) of Eq. (34) at $r_\alpha\geq0$. Further, if the potentials $U_\alpha(r_\alpha)$ are not singular, the function $f_\alpha(r_\alpha)$ in the vicinity of $r_{\alpha0}$ can be expanded into a power series:

$$f_\alpha(r_\alpha)=f_\alpha(r_{\alpha0})+(\omega_\alpha/2)(r_\alpha-r_{\alpha0})^2+\cdots, \qquad (35)$$

where

$$\omega_\alpha=d^2f_\alpha(r_\alpha)/dr_\alpha{}^2\,|_{r\alpha=r\alpha_0}>0.$$

The first term $f_\alpha(r_{\alpha0})$ of the series (35) is fixed by normalization of the wavefunctions $\varphi_{n\alpha}(r_\alpha)$ and the rejected terms in the main region $|r_\alpha-r_{\alpha0}|\leq(\hbar/\omega_\alpha)^{1/2}$ in virtue of the Eqs. (10) have a relative order:

$$\left|\frac{(r_\alpha-r_{\alpha0})[dU_\alpha(r_{\alpha0})/dr_{\alpha0}]}{\mathcal{E}_\alpha-U_\alpha(r_{\alpha0})}\right| \approx\left|\left(\frac{\hbar}{M\omega_\alpha}\right)^{1/2}\frac{M^{1/2}dU_\alpha(r_\alpha)/dr_\alpha}{\mathcal{E}_\alpha-U_\alpha(r_{\alpha0})}\right|.$$

Since $dU_\alpha(r_\alpha)/dr_\alpha\propto(M)^{-1/2}$, the series (35) at $M\rightarrow\infty$ and fixed energy $\mathcal{E}_\alpha$ converge rapidly. Thus it is possible to restrict oneself to the terms of the series written in (35). This procedure can be compared with the evaluation of the integral in (32) by the saddle point method. On the other hand, it corresponds to the conventional description of diatomic molecules by means of either the rigid oscillator functions, when $\Pi_{n\alpha}(r_\alpha)$ is expressed in terms of Hermite polynomials $H_{n\alpha}$:

$$\begin{aligned} \exp[-\hbar^{-1}f(r_{\alpha0})]\Pi_{n\alpha}(r_\alpha) = {} & (\omega_\alpha/\pi\hbar)^{1/4}(2^{n_\alpha}n_\alpha!)^{-1/2} \\ & \times H_{n\alpha}[(r_\alpha-r_{\alpha0})(\omega_\alpha/\hbar)^{1/2}] \qquad (36) \end{aligned}$$

or by the spherical oscillator functions, when $r_{\alpha0}=0$ and $\Pi_{n\alpha}(r_\alpha)$ are expressed in terms of Laguerre polynomials $\mathfrak{L}_{n\alpha}{}^{l\alpha+1/2}$:

$$\begin{aligned} & \exp[-\hbar^{-1}f(r_{\alpha0})]\Pi_{n\alpha}(r_\alpha) \\ & \quad =(\omega_\alpha/\pi\hbar)^{1/4}[n_\alpha!\Gamma(l_\alpha+n_\alpha+\tfrac{3}{2})]^{-1/2} \\ & \quad \times[r_\alpha{}^2(\omega_\alpha/\hbar)]^{(l\alpha+1)/2}\mathfrak{L}_{n\alpha}{}^{l\alpha+1/2}(r_\alpha{}^2\omega_\alpha/\hbar). \qquad (37) \end{aligned}$$

The energy levels are expressed in terms of the quantum numbers n_α, l_α in the cases of (36) and (37), respectively, by means of the formulas

$$\mathcal{E}_\alpha=U_\alpha(r_{\alpha0})+[\hbar^2l_\alpha(l_\alpha+1)/r_{\alpha0}{}^2]+(n_\alpha+\tfrac{1}{2})\hbar\omega_\alpha, \qquad (36')$$

$$\mathcal{E}_\alpha=U_\alpha(0)+(2n_\alpha+l_\alpha+\tfrac{3}{2})\hbar\omega_\alpha. \qquad (37')$$

It should be noted that (36) is applicable only at $r_{\alpha0}>0$ and does not give the correct behavior of the wavefunctions at zero $r_\alpha=0$. This is consistent with the fact that the asymptotes of the integrals (32) in the heavy mass limit and finite l_α should be considered at the conditions

$$r_{\alpha0}{}^2\gg l_\alpha{}^2\hbar/\omega_\alpha \qquad (38)$$

since $r_{\alpha0}\propto M^{1/2}$. When the inverse inequalities are valid, we obtain the best description by using the spherical oscillator functions given by Expression (37).

Both examples of the wavefunctions $\varphi_{n\alpha}(r_\alpha)$ considered above are characterized by the fact (which will be made use of later on) that they contain the factor $\exp[-(\omega_\alpha/2\hbar)(r_\alpha-r_{\alpha0})^2]$ giving the localization of the functions of the bound states in the region $|r_\alpha-r_{\alpha0}|\leq$

$(\hbar/\omega_\alpha)^{1/2}$. In further calculations significantly different results are obtained when the wavefunctions $\varphi_{n\alpha}$ decrease with increasing r_α so slowly that the transition potential $\mathcal{V}_0 \exp[-(\rho_i r_i+\rho_f r_f)]$ becomes the main cutting-off factor under the integrals (32). A similar behavior of the expressions for the cross sections is also realized when $f_\alpha(r_\alpha)$ in (35) proves to be a linear function of r_α, as is the case for Coulombic interaction.

The wavefunctions $\varphi_{n\alpha}(r_\alpha)$ decrease to zero as $r_\alpha{}^{l_\alpha+1}$ in the case of nonsingular potentials $U_\alpha(r_\alpha)$ and more rapidly in the case of the potentials $U_\alpha(r_\alpha)$ with a repulsive core.[17]

Let us pass now to the choice of the functions $\chi_{L\alpha}{}^{\pm}(R_\alpha)$. In calculating the integrals (32), one must be especially careful because these functions do not diminish at infinity. Violation of the correct behavior of these functions at infinity can lead to qualitatively incorrect conclusions. To solve the problem arising here, in the next section we shall consider two model cases: (a) the case of the potentials $W_\alpha(R_\alpha)$ being equal to zero and (b) the case of hard sphere potential. Each of these reflects certain features of real intermolecular interactions at different values of R_α.

IV. DETERMINATION OF THE REACTION CROSS SECTIONS FOR MODEL POTENTIALS

Let us consider the first model case of vanishing potentials $W_\alpha(R_\alpha)=0$, i.e., when Eqs. (24) are valid. The easiest way of performing calculations here would be to use Formula (25). Let us go over by means of Eqs. (4) to the integration variables $\mathbf{r}_i$, $\mathbf{r}_f$. As the result we have

$$T^0(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i) = -(\mathcal{V}_0/\sin^3\eta) \int d^3r_i d^3r_f \biggl\{ \exp[(i/\hbar)(q_f r_f - q_i r_i)] \times \frac{\varphi_{n_f}(r_f)}{r_f} Y_{l_f m_f}{}^*(\hat{\mathbf{r}}_f) \exp[-(\rho_i r_i+\rho_f r_f)] \frac{\varphi_{n_i}(r_i)}{r_i} Y_{l_i m_i}(\hat{\mathbf{r}}_i) \biggr\}. \tag{39}$$

We have introduced the "transferred" momenta:

$$q_i = (1/\sin\eta)(\mathbf{k}_f - \mathbf{k}_i \cos\eta), \qquad q_f = (1/\sin\eta)(k_i - k_f \cos\eta). \tag{40}$$

Using the expansion (26) and performing integration over the angles, we obtain

$$T^0(\theta \mid l_f, m_f, n_f; k_i, l_i, m_i, n_i) = -i^{(l_i-l_f)} \frac{\mathcal{V}_0}{q_i q_f \sin^3\eta} Y_{l_i m_i}(\hat{\mathbf{q}}_i) Y_{l_f m_f}(\hat{\mathbf{q}}_f) \times \int_0^\infty dr_f \int_0^\infty dr_i \biggl\{ \left(\frac{q_i r_i}{\hbar}\right)^{1/2} J_{l_i+1/2}\left(\frac{q_i r_i}{\hbar}\right) \left(\frac{q_f r_f}{\hbar}\right)^{1/2} J_{l_f+1/2}\left(\frac{q_f r_f}{\hbar}\right) \exp[-(\rho_i r_i+\rho_f r_f)] \varphi_{n_i}(r_i) \varphi_{n_f}(r_f) \biggr\}. \tag{41}$$

It is clear from (41) that the determination of the scattering matrix reduces to finding the Hankel transforms $\varphi_{n\alpha}(q_\alpha)$ [multiplied by $\exp(-\rho_\alpha r_\alpha)$] of the radial wavefunctions of the bound states:

$$\begin{aligned}\varphi_{n\alpha}(q_\alpha) &= \int_0^\infty dr_\alpha \biggl\{ \left(\frac{q_\alpha r_\alpha}{\hbar}\right)^{1/2} J_{l\alpha+1/2}\left(\frac{q_\alpha r_\alpha}{\hbar}\right) \varphi_{n\alpha}(r_\alpha) \exp(-\rho_\alpha r_\alpha) \biggr\} \\ &= \tfrac{1}{2} \operatorname{Re} \int_0^\infty dr_\alpha \biggl\{ \left[r_\alpha{}^{l_\alpha+1} \left(\frac{q_\alpha r_\alpha}{\hbar}\right)^{1/2} \mathcal{H}_{l\alpha+1/2}{}^{(1)}\left(\frac{q_\alpha r_\alpha}{\hbar}\right) \right] \frac{\varphi_{n\alpha}(r_\alpha)}{r_\alpha{}^{l_\alpha+1}} \exp(-\rho_\alpha r_\alpha) \biggr\}. \end{aligned} \tag{42}$$

The expression in square brackets is in the integral of the form

$$r_\alpha{}^{l_\alpha+1} \left(\frac{q_\alpha r_\alpha}{\hbar}\right)^{1/2} \mathcal{H}_{l\alpha+1/2}{}^{(1)}\left(\frac{q_\alpha r_\alpha}{\hbar}\right) = \left(\frac{2}{\pi}\right)^{1/2} \frac{i^{-(l_\alpha+1)} \hbar^{l_\alpha+1}}{q_\alpha{}^{l_\alpha+1}} r_\alpha \exp\left(\frac{i q_\alpha r_\alpha}{\hbar}\right) \times \sum_{k=0}^{l_\alpha} (\tfrac{1}{2} i)^k \frac{(l_\alpha+k)!}{k!(l_\alpha-k)!} (r_\alpha)^{l_\alpha-k} \left(\frac{q_\alpha}{\hbar}\right)^{-k}. \tag{43}$$

Thus (42) is the integral of the product of three factors: the exponential $\exp(iq_\alpha r_\alpha/\hbar)$, a polynomial of r_α, and the regular function $(r_\alpha)^{-(l_\alpha+1)}\varphi_{n\alpha}(r_\alpha)\exp(-\rho_\alpha r_\alpha)$. Substituting into (42) the functions $\varphi_{n\alpha}(r_\alpha)$ in the form (33), retaining only the written terms of the expansion (35), we obtain

$$\varphi_{n\alpha}(q_\alpha) = \tfrac{1}{2} \operatorname{Re} \int_0^\infty dr_\alpha \biggl\{ \tilde{\Pi}_{n\alpha}(r_\alpha) \exp\left(\frac{i q_\alpha r_\alpha}{\hbar} - \frac{\omega_\alpha}{2\hbar}(r_\alpha - r_{\alpha 0})^2 - \rho_\alpha r_\alpha \right) \biggr\}, \tag{44}$$

where $\tilde{\Pi}_{n\alpha}(r_\alpha)$ is a certain new polynomial of r_α. Expression (44) can be transformed to the form

$$\varphi_{n\alpha}(q_\alpha)=\tfrac{1}{2}\operatorname{Re}\exp\left[-\frac{(q_\alpha+\hbar\rho_\alpha)^2}{2\omega_\alpha}+i\left(\frac{q_\alpha}{\hbar}+i\rho_\alpha\right)r_{\alpha0}\right]$$

$$\times\int_{-r_{\alpha0}+(iq_\alpha/\hbar w_\alpha)}^{\infty+(iq_\alpha/\hbar w_\alpha)}dr_\alpha\left\{\tilde{\Pi}_{n\alpha}\left(r_\alpha+r_{\alpha0}-\frac{(iq_\alpha-\hbar\rho_\alpha)}{\omega_\alpha}\right)\exp\left(-\frac{\omega_\alpha}{2\hbar}r_\alpha^2\right)\right\}\tag{45}$$

and the integral is to be taken in the general case. In particular, at $\rho_\alpha\ll(\omega_\alpha/\hbar)^{1/2}$ we find, taking account of (36) and (38), that for a rigid oscillator the following equation is valid:

$$\varphi_{n\alpha}(q_\alpha)\approx2(\hbar/\pi\omega_\alpha)^{1/4}(2^{n\alpha}n_\alpha!)^{-1/2}(q_\alpha^2/\hbar\omega_\alpha)^{n\alpha/2}\exp(-q_\alpha^2/2\hbar\omega_\alpha)\cos[(q_\alpha r_{\alpha0}/\hbar)+\tfrac{1}{2}\pi(n_\alpha-l_\alpha-1)].\tag{46}$$

For a spherical oscillator at $\rho_\alpha\ll(\omega_\alpha/\hbar)^{1/2}$ the following equation is valid:

$$\varphi_{n\alpha}(q_\alpha)\approx(\hbar/\pi\omega_\alpha)^{1/4}(q_\alpha^2/\hbar\omega_\alpha)^{l\alpha+1}[2^{4(l\alpha+1)}n_\alpha!\Gamma(l_\alpha+n_\alpha+\tfrac{3}{2})]^{1/2}\exp(-q_\alpha^2/2\hbar\omega_\alpha)\mathfrak{L}_{n\alpha}{}^{l\alpha+1/2}(q_\alpha^2/\hbar\omega_\alpha).\tag{47}$$

Expressions (46) and (47) have the following important properties that are not connected with the concrete choice of the functions $\varphi_{n\alpha}(r_\alpha)$. First, both these expressions contain the factor $\exp(-q_\alpha^2/2\hbar\omega_\alpha)$ responsible for rapid decrease of $\varphi_{n\alpha}(q_\alpha)$ at $q_\alpha^2>\hbar\omega_\alpha$. This factor is evidently related to the localization of the wavefunction of the bound state $\varphi_{n\alpha}(r_\alpha)$. Second, Expression (47) contains the factor $(q_\alpha^2/\hbar\omega_\alpha)^{(l\alpha+1)/2}$ responsible for the decrease of $\varphi_{n\alpha}(q_\alpha)$ at small q_α. There is no such factor in (46) for the only reason that when calculating this expression we used the inequalities (38). Evidently, the appearance of this factor is due to the general threshold behavior of the regular wavefunctions $\varphi_{n\alpha}(r_\alpha)$, which follows directly from (42) with the help of the expansion of the Bessel function into a power series. It is obvious from the above reasoning that the basic dependence $\varphi_{n\alpha}(q_\alpha)$ in the important range of q_α is given by the expressions

$$\varphi_{n\alpha}(q_\alpha)=A_\alpha(q_\alpha^2/\hbar\omega_\alpha)^{(l\alpha+1)/2}\exp(-q_\alpha^2/2\hbar\omega_\alpha).\tag{48}$$

The coefficient A_α in (48) includes the factors polynomially dependent on q_α and also on the oscillating factors. In the heavy mass limit, the former can be considered to be approximately constant, and the latter to oscillate fast and ultimately give a constant when the cross section—the square of the amplitude modulus—is averaged over a small initial momenta range. Expression (48) has a right symmetry when q_α is substituted by $-q_\alpha$.

A result essentially different from (48) is obtained when the wavefunctions $\varphi_{n\alpha}(r_\alpha)$ decrease so slowly that $\exp[-(\rho_ir_i+\rho_fr_f)]$ becomes the main cutting factor in the integral (42). A similar result is obtained when $f_\alpha(r_\alpha)$ in (38) is linear with respect to r_α, as is the case in Coulombic interaction. Substituting in such cases the wavefunctions $\varphi_{n\alpha}(r_\alpha)$ in (42) by their threshold expressions, we obtain

$$\varphi_{n\alpha}(q_\alpha)\approx\int_0^\infty dr_\alpha\left\{r_\alpha{}^{l\alpha+1}\left(\frac{q_\alpha r_\alpha}{\hbar}\right)^{1/2}J_{l\alpha+1/2}\left(\frac{q_\alpha r_\alpha}{\hbar}\right)\exp(-\rho_\alpha r_\alpha)\right\}$$

$$=2^{l\alpha+3/2}\pi^{-1/2}[(l_\alpha+2)!\hbar\rho_\alpha q_\alpha{}^{l\alpha+1}/(\hbar^2\rho_\alpha^2+q_\alpha^2)^{l\alpha+2}],\tag{49}$$

i.e., here $\varphi_{n\alpha}(q_\alpha)$ not only does not decrease but, on the contrary, increases with rising l_α at small (but larger than ρ_α) q_α.

The reaction cross section is expressed in terms of the functions $\varphi_{n\alpha}(q_\alpha)$ examined above. By averaging over the initial momentum projections m_i and by summation over the final momentum projections m_f, from (21) and (41) we obtain

$$\sigma^0(\theta\mid l_f,n_f;k_i,l_i,n_i)\equiv(2l_i+1)^{-1}\sum_{m_im_f}\sigma(\theta\mid l_f,m_f,n_f;k_i,l_i,m_i,n_i)=(16\pi^2)^{-1}(k_f\mathfrak{V}_0^2/k_iq_i^2q_f^2)$$

$$\times[M/m_2(m_1+m_2)\sin^6\eta][(2l_f+1)/(2l_i+1)]^{1/2}\mid\varphi_{n_i}(q_i)\varphi_{n_f}(q_f)\mid^2.\tag{50}$$

Here we have used Eq. (16):

$$\sum_{m_\alpha}Y_{lama}{}^*(\hat{\mathbf{q}}_\alpha)Y_{lama}(\hat{\mathbf{q}}_\alpha)=(2l_\alpha+1)/4\pi.$$

For localized bound states the cross section σ^0 is maximum in the direction $\theta=\theta_{\text{opt}}{}^0\equiv0$ when according to (48) and (40)

$$\sigma^0(\theta=0)\propto\exp\{-(\sin^2\eta)^{-1}[(k_f-k_i\cos\eta)^2/\hbar\omega_i+(k_i-k_f\cos\eta)^2/\hbar\omega_f]\}.\tag{51}$$

At $q_\alpha<\hbar\omega_\alpha$ the cross section behaves as

$$\sigma\propto(q_i^2/\hbar\omega_i)^{(l_i+1)/2}(q_f^2/\hbar\omega_f)^{(l_f+1)/2}.\tag{51'}$$

Further analysis of Expression (50) we shall put off until the next section. Now we shall pass on to the consideration of the second model case of the hard sphere potentials when

$$
\begin{aligned}
W_\alpha(R_\alpha)=W_\alpha{}^{\mathrm{H.C.}}(R_\alpha)&\equiv 0 \quad \text{at} \quad R_\alpha>R_{\alpha 0}\\
&\equiv \infty \quad \text{at} \quad R_\alpha\leq R_{\alpha 0},\\
\chi_{L_\alpha}{}^{+}(R_\alpha)=\chi_{L_\alpha}{}^{+\mathrm{H.C.}}(R_\alpha)&\equiv(\pi R_\alpha/2)^{1/2}\mathcal{H}_{L_\alpha+1/2}{}^{(1)}(k_\alpha R_\alpha/\hbar)\,\theta(R_\alpha-R_{\alpha 0}),\\
\chi_{L_\alpha}{}^{-}(R_\alpha)=\chi_{L_\alpha}{}^{-\mathrm{H.C.}}(R_\alpha)&\equiv(\pi R_\alpha/2)^{1/2}\mathcal{H}_{L_\alpha+1/2}{}^{(2)}(k_\alpha R_\alpha/\hbar)\,\theta(R_\alpha-R_{\alpha 0}),\\
\exp(2i\delta_{L_\alpha}{}^{\mathrm{H.C.}})&=-\mathcal{H}_{L_\alpha+1/2}{}^{(2)}(k_\alpha R_{\alpha 0}/\hbar)\,[\mathcal{H}_{L_\alpha+1/2}{}^{(1)}(k_\alpha R_{\alpha 0}/\hbar)]^{-1}.
\end{aligned}
\tag{52}
$$

Where H.C. denotes "hard core." Substitution of (52) in (32) gives for the reaction amplitude the expression

$$
\begin{aligned}
T^{\mathrm{H.C.}}(L_f,l_f,m_f,n_f;k_i,L_i,l_i,m_i,n_i)=&-\frac{\mathcal{V}_0}{\sin^3\eta(k_ik_f)}\sum_{JM\mu}\left\{\frac{8\pi^2}{2J+1}\left(\frac{2L_i+1}{4\pi}\right)^{1/2}C(L_f,l_f,J;m_i-m_f,m_f)\right.\\
&\times C(L_i,l_i,J;0,m_i)C(L_i,l_i,J;0,M)C(L_f,l_f,J;\mu,M-\mu)Y_{L_f\mu}(\theta,0)\\
&\times\int_{-1}^{1}d\cos\beta\int_{R_{f0}}^{\infty}R_fdR_f\int_{R_{i0}}^{\infty}R_idR_i[(r_ir_f)^{-1}Y_{L_f\mu}{}^*(\beta,0)Y_{l_f,M-\mu}{}^*(\gamma_f,0)Y_{l_iM}(\gamma_i,0)\varphi_{n_f}(r_f)\varphi_{n_i}(r_i)]\\
&\times\left[-\left(\frac{\mathcal{H}_{L_f+1/2}{}^{(2)}(k_fR_{f0}/\hbar)}{\mathcal{H}_{L_f+1/2}{}^{(1)}(k_fR_{f0}/\hbar)}+1\right)\left(\frac{k_fR_f}{\hbar}\right)^{1/2}\mathcal{H}_{L_f+1/2}{}^{(1)}\left(\frac{k_fR_f}{\hbar}\right)+2\left(\frac{k_fR_f}{\hbar}\right)^{1/2}J_{L_f+1/2}\left(\frac{k_fR_f}{\hbar}\right)\right]\\
&\left.\times\left[-\left(\frac{\mathcal{H}_{L_i+1/2}{}^{(2)}(k_iR_{i0}/\hbar)}{\mathcal{H}_{L_i+1/2}{}^{(1)}(k_iR_{i0}/\hbar)}+1\right)\left(\frac{k_iR_i}{\hbar}\right)^{1/2}\mathcal{H}_{L_i+1/2}{}^{(1)}\left(\frac{k_iR_i}{\hbar}\right)+2\left(\frac{k_iR_i}{\hbar}\right)^{1/2}J_{L_i+1/2}\left(\frac{k_iR_i}{\hbar}\right)\right]\right\}.
\end{aligned}
\tag{52'}
$$

Substitution of the above expression in (22) gives the formula for the cross sections at all values of the parameters. Let us analyze the results obtained in the heavy mass limit. For the elastic scattering amplitudes $t_{L_\alpha}{}^{\mathrm{H.C.}}(k_\alpha)$ contained in (52) in the limiting case mentioned, in view of the properties of the Bessel functions, the following relations are valid:

$$
t_{L_\alpha}{}^{\mathrm{H.C.}}(k_\alpha)=-\frac{\hbar}{2ik_\alpha}\left[\frac{\mathcal{H}_{L_\alpha+1/2}{}^{(2)}(k_\alpha R_{\alpha 0}/\hbar)}{\mathcal{H}_{L_\alpha+1/2}{}^{(1)}(k_\alpha R_{\alpha 0}/\hbar)}+1\right]\approx\begin{cases}=0 \quad \text{at} \quad L_\alpha>k_\alpha R_{\alpha 0}/\hbar\\ =(\hbar/2ik_\alpha)\{(-1)^{L_\alpha}\exp[-2i(k_\alpha R_{\alpha 0}/\hbar)]-1\} \quad \text{at} \quad L_\alpha<k_\alpha R_{\alpha 0}/\hbar.\end{cases}
\tag{53}
$$

The vanishing of the amplitude in (53) at

$$
b_\alpha\equiv\hbar L_\alpha/k_\alpha>R_{\alpha 0}
\tag{54}
$$

has a simple physical interpretation: in the quasiclassical limit the rays corresponding to the impact parameters b_α, larger than radius $R_{\alpha 0}$, do not deviate. It follows from (53) primarily that the functions

$$
(k_\alpha R_\alpha/\hbar)^{1/2}\mathcal{H}_{L_\alpha+1/2}{}^{(1)}(k_\alpha R_\alpha/\hbar)
$$

contained in (52) can be substituted by their asymptotes at $L_\alpha<k_\alpha R_{\alpha 0}/\hbar$:

$$
(k_\alpha R_{\alpha 0}/\hbar)^{1/2}\mathcal{H}_{L_\alpha+1/2}{}^{(1)}(k_\alpha R_{\alpha 0}/\hbar)\approx(\tfrac{1}{2}\pi)^{1/2}\exp(i\{(k_\alpha R_\alpha/\hbar)-[(L_\alpha+1)\pi/2]\}).
\tag{55}
$$

Further it follows from (52) and (53) that if the main contribution to the reaction (both in initial and final channels) is made by the quasiclassical trajectories corresponding to the impact parameters which are larger than the corresponding hard sphere radii, we can simply assume $R_{\alpha 0}=0$. In other words, we return in fact to the case $W_\alpha=0$, considered at the beginning of this section. We can say that the main contribution is made by the trajectories with definite impact parameters in view of the fact that for localized bound states $\varphi_{n_\alpha}(r_\alpha)$ the integrals of the form (52) are defined by the values of the integrands in the regions

$$
\begin{aligned}
R_i&\approx(\sin\eta)^{-1}[(r_{i0}\cos\eta+r_{f0})^2]^{1/2},\\
R_f&\approx(\sin\eta)^{-1}[(r_{i0}+r_{f0}\cos\eta)^2]^{1/2}.
\end{aligned}
\tag{56}
$$

A different situation arises when in the initial or in the final channel, or in both, the impact parameters making the main contribution to the integral (52) satisfy the reverse condition of (54):

$$
b_\alpha\equiv\hbar L_\alpha/k_\alpha<R_{\alpha 0}.
\tag{57}
$$

The inequality (57) is always valid at finite $R_{\alpha 0}$ and k tending to infinity. Let us consider the case when (57) is valid for initial and final channels. Here we can substitute for all Bessel functions contained in the expression for $T^{\mathrm{H.C.}}$ the asymptotes for the argument larger than the index:

$$(k_\alpha R_\alpha/\hbar)^{1/2}\mathcal{H}_{L\alpha+1/2}{}^{(1,2)}(k_\alpha R_\alpha/\hbar)\approx(\tfrac{1}{2}\pi)^{1/2}\exp\{\pm i[(k_\alpha R_\alpha/\hbar)-\tfrac{1}{2}\pi(L_\alpha+1)]\}. \tag{58}$$

Taking account of (53), (58), after substitution of (52) in (22), in the case under consideration we obtain

$$\begin{aligned}
T^{\mathrm{H.C.}}(\theta\,|\,l_f, m_f, n_f; k_i, l_i, m_i, n_i)\approx{}&\frac{\pi^2\mathcal{V}_0(-1)^{l_f-l_i}}{k_ik_f\sin^3\eta}\exp[-(i/\hbar)(k_iR_{i0}+k_fR_{f0})]\\
&\times\sum_{L_fL_iJM\mu}\Bigg\{(-1)^{L_f}\frac{4\pi(2L_i+1)}{2J+1}Y_{L_f,m_i-m_f}(\theta,0)C(L_f,l_f,J;m_i\_m_f,m_f)C(L_i,l_i,J;0,m_i)\\
&\times C(L_f,l_f,J;\mu,M-\mu)C(L_i,l_i,J;0,M)\int_{-1}^{1}d\cos\beta\int_0^\infty dR_f\int_0^\infty dR_i\Bigg[\frac{R_iR_f}{r_ir_f}\,\theta(R_i^2-R_{i0}^2)\theta(R_f^2-R_{f0}^2)\\
&\times Y_{L_f,\mu}{}^*(\beta,0)\,Y_{l_f,M-\mu}{}^*(\gamma_f,0)\,Y_{l_iM}(\gamma_i,0)\exp[-(\rho_ir_i+\rho_fr_f)]\\
&\times\varphi_{n_i}(r_i)\varphi_{n_f}(r_f)\sin\frac{k_i(R_i-R_{i0})}{\hbar}\sin\frac{k_f(R_f-R_{f0})}{\hbar}\Bigg]\Bigg\}.
\end{aligned}\tag{59}$$

In writing Eq. (59) we used the parity conservation law. For the sums over J and L_i contained in (59) the following equality is valid[16]:

$$\begin{aligned}
&\sum_{JL_i}[(2L_i+1)/(2J+1)C(L_f,l_f,J;m_i-m_f,m_f)C(L_i,l_i,J;0,m_i)C(L_f,l_f,J;\mu,M-\mu)C(L_i,l_i,J;0,M)]\\
&\quad=(-1)^{m_i+M}\sum_{JL_i}[C(J,l_i,L_i;-M,0)C(J,l_i,L_i;-m_i,0)C(L_f,l_f,J;m_i-m_f,m_f)C(L_f,l_f,J;\mu,M-\mu)]\\
&\quad=\delta_{Mm_i}\sum_J[C(L_f,l_f,J;m_i-m_f,m_f)C(L_f,l_f,J;\mu,m_i-\mu)]\\
&\quad=\delta_{Mm_i}\delta_{\mu,m_i-m_f}.
\end{aligned}$$

By means of this equality, from (59) we obtain in the heavy mass limit

$$\begin{aligned}
T^{\mathrm{H.C.}}\approx{}&(-1)^{l_f-l_i}\frac{4\pi^3}{k_ik_f\sin^3\eta}\exp\left(-i\frac{k_iR_{i0}+k_fR_{f0}}{\hbar}\right)\sum_{L_fM_f}\Bigg\{(-1)^{L_f}Y_{L_fM_f}(\theta,0)(2\pi)^{-1}\\
&\times\int_0^{2\pi}d\alpha\int_{-1}^{1}d\cos\beta\int_0^\infty dR_f\int_0^\infty dR_i\Bigg[\frac{R_fR_i}{r_ir_f}\,\theta(R_i^2-R_{i0}^2)\theta(R_f^2-R_{f0}^2)\,Y_{L_fM_f}{}^*(\beta,\alpha)\,Y_{l_fm_f}{}^*(\gamma_f,\alpha)\\
&\times Y_{l_im_i}(\gamma_i,\alpha)\varphi_{n_i}(r_i)\varphi_{n_f}(r_f)\exp[-(\rho_ir_i+\rho_fr_f)]\sin\frac{k_i(R_i-R_{i0})}{\hbar}\sin\frac{k_f(R_f-R_{f0})}{\hbar}\Bigg]\Bigg\}\\
={}&(-1)^{l_f-l_i}\frac{2\pi^2V_0}{k_ik_f\sin^3\eta}\exp\left(-i\frac{k_iR_{i0}+k_fR_{f0}}{\hbar}\right)\int_0^\infty dR_f\int_0^\infty dR_i\\
&\times\Bigg\{\frac{R_fR_i}{r_fr_i}\,\theta(R_i^2-R_{i0}^2)\theta(R_f^2-R_{f0}^2)\sin\frac{k_f(R_f-R_{f0})}{\hbar}\sin\frac{k_i(R_i-R_{i0})}{\hbar}\\
&\times Y_{l_fm_f}{}^*(\gamma_f,\pi)\,Y_{l_im_i}(\gamma_i,\pi)\varphi_{n_i}(r_i)\varphi_{n_f}(r_f)\exp[-(\rho_ir_i+\rho_fr_f)]\Bigg\}\Bigg|_{\beta=\theta-\pi}.
\end{aligned}\tag{60}$$

In writing (60) we introduced summation over M_f and integration with respect to α, which compensate each other since the integral with respect to α is equal to the Kronecker symbol δ_{M_f,m_i-m_f} multiplied by 2π. Thus we are able to use the equality from the spherical harmonics theory:

$$\begin{aligned}
\sum_{LM}(-1)^LY_{LM}(\theta,0)\,Y_{LM}{}^*(\beta,\alpha)={}&\sum_{LM}Y_{LM}(\theta-\pi,\pi)\,Y_{LM}{}^*(\beta,\alpha)\\
={}&\delta[\cos(\theta-\pi)-\cos\beta]\delta(n-\pi).
\end{aligned}$$

This equality follows from the completeness of the set of spherical harmonics and their orthogonality and also from the equation

$$(-1)^L Y_{LM}(\theta, 0) = Y_{LM}(\theta-\pi, \pi).$$

The θ functions contained in the integral (60) can be expressed with the help of Formulas (4) and (31) in terms of the variables r_α and δ:

$$\theta(R_i^2-R_{i0}^2) = \theta(r_i^2 \cos^2\eta + 2r_i r_f \cos\eta \cos\delta + r_f^2 - R_{i0}^2 \sin^2\eta),$$

$$\theta(R_f^2-R_{f0}^2) = \theta(r_i^2 + 2r_i r_f \cos\eta \cos\delta + r_f^2 \cos^2\eta - R_{f0}^2 \sin^2\eta). \tag{61}$$

The inequalities (57) are realized in the main integration range in (60) in the case of the wavefunctions of bound states localized in the range of such values of $r_i \approx r_{i0}$, $r_f \approx r_{f0}$ for which either separately, or simultaneously, the following conditions are valid:

$$r_{i0}^2 \cos^2\eta + 2r_{i0} r_{f0} \cos\delta \cos\eta + r_{f0}^2 \lesssim R_{i0}^2 \sin^2\eta,$$

$$r_{i0}^2 + 2r_{i0} r_{f0} \cos\delta \cos\eta + r_{f0}^2 \cos^2\eta \lesssim R_{f0}^2 \sin^2\eta. \tag{62}$$

Hence it follows that under the condition of sufficiently rigid localization of bound states, the integral (60) assumes a nonvanishing value only at δ close to zero. According to Eqs. (30) and (31), δ can be equal to zero only at $\beta = 0$. In the integral (60), β is equal to zero at $\theta = \pi$. Thus when (57) is valid, the reaction products scatter mainly in the backward direction. The physical reason for this phenomenon is simple enough: at impact parameters less than the hard sphere radius, the quasiclassical trajectories of elastic scattering are directed backwards.

For brevity, let us examine the form of the scattering amplitude (60) only for the optimum direction $\theta = \theta_{\text{opt}}^{\text{H.C.}} \equiv \pi$. In this case,

$$T^{\text{H.C.}}(\theta=\pi) = (-1)^{l_f+m_f-l_i-m_i} \frac{2\pi^2 \mathcal{V}_0}{k_i k_f \sin^3\eta} \exp[-(i/\hbar)(k_i R_{i0} + k_f R_{f0})]$$

$$\times \int_0^\infty dR_f \int_0^\infty dR_i \left\{ \frac{R_i R_f}{|r_i||r_f|} \theta(R_i^2 - R_{i0}^2)\theta(R_f^2 - R_{f0}^2) \sin \frac{k_i(R_i - R_{i0})}{\hbar} \right.$$

$$\left. \times \sin \frac{k_f(R_f - R_{f0})}{\hbar} \varphi_{n_i}(|r_i|)\varphi_{n_f}(|r_f|) \exp[-(\rho_i |r_i| + \rho_f |r_f|)] \right\}, \tag{63}$$

where r_α and R_α are now related by the formulas corresponding to $\theta = \pi$:

$$R_i = (\sin\eta)^{-1}(R_f - R_i \cos\eta), \qquad R_i = (\sin\eta)^{-1}(r_i \cos\eta + r_f),$$

$$r_f = (\sin\eta)^{-1}(R_i - R_f \cos\eta), \qquad R_f = (\sin\eta)^{-1}(r_f \cos\eta + r_i). \tag{64}$$

Let us take functions of the bound states in the forms (33) and (35) and transform in (63) to the integration variables r_α. We shall also assume the reaction to occur at distances from the sphere boundary larger than the scale of localization of the wavefunctions of bound states:

$$(r_{i0} \cos\eta + r_{f0}) - R_{i0} > (\hbar/\omega_i)^{1/2},$$

$$(r_{i0} + r_{f0} \cos\eta) - R_{f0} > (\hbar/\omega_f)^{1/2}. \tag{65}$$

The conditions (65) are always valid in the limit $\hbar \to 0$. When (65) is valid, the integration range in (63) is effectively cut off by the functions of the bound states. Consequently, after changing the variables and using Eqs. (33) and (35), we can approximately equate

$$T^{\text{H.C.}}(\theta=\pi) \approx (-1)^{(l_f+m_f)-(l_i+m_i)} \frac{2\pi^2 \mathcal{V}_0}{k_i k_f \sin^4\eta} \exp\left(-\frac{i}{\hbar}(k_i R_{i0} + k_f R_{f0})\right) \int_{-\infty}^\infty dr_i \int_{-\infty}^\infty dr_f$$

$$\times \left\{ \frac{(r_{i0}^2 + r_{f0}^2)\cos\eta + r_{i0} r_{f0}(1+\cos^2\eta)}{r_{i0} r_{f0}} \exp[-(\rho_i r_{i0} + \rho_f r_{f0})] \Pi_i(r_{i0}) \Pi_f(r_{f0}) \exp\left(-\frac{\omega_i(r_i - r_{i0})^2}{2\hbar} - \frac{\omega_f(r_f - r_{f0})^2}{2\hbar}\right) \right.$$

$$\left. \times \sin\left[\frac{k_i}{\hbar}\left(\frac{r_f + r_i \cos\eta}{\sin\eta} - R_{i0}\right)\right] \sin\left[\frac{k_f}{\hbar}\left(\frac{r_i + r_f \cos\eta}{\sin\eta} - R_{f0}\right)\right] \right\}. \tag{66}$$

Here as before we assume $\hbar\rho_\alpha^2 \ll \omega_\alpha$. Equation (66) contains with different constant and phase factors the integrals of the kind

$$\int_{-\infty}^{\infty} dr_i \int_{-\infty}^{\infty} dr_f \left\{\exp\left[\pm\frac{i}{\hbar}\frac{k_f}{\sin\eta}(r_i+r_f\cos\eta)\pm\frac{i}{\hbar}\frac{k_i}{\sin\eta}(r_f+r_i\cos\eta)-\frac{\omega_i(r_i-r_{i0})^2}{\hbar}-\frac{\omega_f(r_f-r_{f0})^2}{\hbar}\right]\right\}. \qquad (67)$$

These integrals, with the accuracy within constant and phase factors, are proportional to the quantities

$$\exp\{-[(k_i\pm k_f\cos\eta)^2/2\hbar\omega_f\sin^2\eta]-[(k_f\pm k_i\cos\eta)^2/2\hbar\omega_i\sin^2\eta]\}. \qquad (68)$$

Retaining only the largest terms with the squares of differences in the index of the exponentials (68) we obtain

$$\sigma^{\mathrm{H.C.}}(\theta=\theta_{\mathrm{opt}}{}^{\mathrm{H.C.}}\equiv\Pi)\approx\exp[-(k_i-k_f\cos\eta)^2/\hbar\omega_f\sin^2\eta-(k_f-k_i\cos\eta)^2/\hbar\omega_i\sin^2\eta]. \qquad (69)$$

From comparison of (69) with (51), a very important fact follows, i.e., the basic functional dependence of the reaction cross section in the optimum direction on the momentum moduli (i.e., kinetic energies) is the same for both cases considered in this section.

It should be stressed in conclusion that the expressions for the cross sections of the form (69) are obtained when the transferred momenta q_α are not too small, in particular at $q_\alpha \gtrsim (\hbar\omega_\alpha)^{1/2}$. When the inverse inequalities are valid, we return to the threshold formulas (51′) for small values of $\mathcal{V}_\alpha$.

V. ANALYSIS OF THE EXPRESSIONS FOR THE REACTION CROSS SECTION

From the consideration in previous sections, it is possible to draw some conclusions regarding the basic general properties of cross sections and show the methods of their calculation. Let us first consider the choice of the radial functions $\chi_{L_\alpha}{}^{\pm}(R_\alpha)$ to be substituted in (23) and (32). It is known that in intermolecular interactions in most cases there exists an effective repulsive core at the distances at which the overlapping of electron shells starts. Accordingly, even at sufficiently large momenta k_α there are turning points determined without taking into account the centrifugal barrier as the solutions of the equation

$$W_\alpha(R_\alpha)+\tfrac{1}{2}k_\alpha^2=0. \qquad (70)$$

These turning points $R_{\alpha 0}(k_\alpha)$, which can be called effective radii of repulsive spheres, depend relatively slightly on the energy $\frac{1}{2}k_\alpha^2$. They should be introduced as the lower integration limits with respect to R_α instead of the quantities $R_{\alpha 0}$ used in the case of the hard sphere potentials. Here only the fraction of the contribution of the tunnel region of radial motion that is associated with the centrifugal barrier is retained. If all possible arrangements of the equilibrium distances are less than $R_{\alpha 0}(k_\alpha)$, the calculation should be of course altered to take proper account of the essentially quantum tunnel region $R_\alpha < R_{\alpha 0}(k_\alpha)$. However, in such a case the reaction cross section becomes vanishingly small, with the exception, possibly, of the hydrogen isotope reactions and the reactions of atoms such as positronium and μ^+ mesonium. By analogy with (55), the wavefunctions in (22) can best be written as

$$\chi_{L_\alpha}{}^{(+)}(R_\alpha)\approx\left[\frac{\hbar}{(k_\alpha^2-2W_\alpha(R_\alpha))^{1/2}}\right]^{1/2} \times\exp\left[\frac{i}{\hbar}\left(k_\alpha R_\alpha-\tfrac{1}{2}(\pi\hbar)(L_\alpha+1) -\int_{R_\alpha}^{\infty}\{[k_\alpha^2-2W_\alpha(R_\alpha)]^{1/2}-k_\alpha\}dR_\alpha\right)\right], \qquad R_\alpha>R_{\alpha 0}. \qquad (71)$$

The choice of (71) corresponding to a special WKB approximation is justified here because the coefficient $t_{L_\alpha}\propto\exp(2i\delta_{L_\alpha})-1$ before $\chi_{L_\alpha}{}^{+}(R_\alpha)$ for short range potentials in a quasiclassical limit decreases fast (as in Fraunhofer diffraction[17,18]) at the impact parameters b_α lesser than $R_{\alpha 0}(k)$. In the heavy mass limit another combination of the functions $\chi_{L_\alpha}{}^{+}(R_\alpha)+\chi_{L_\alpha}{}^{-}(R_\alpha)$ contained in (23) at $R_\alpha > R_{\alpha 0}(k)$ may be taken in the form corresponding to the eikonal approximation,[17] i.e., in the form corresponding to the expansion in spherical waves of the plane wave with a momentum corrected for the influence of the potentials $W_\alpha(R_\alpha)$:

$$[\chi_{L_\alpha}{}^{+}(R_\alpha)+\chi_{L_\alpha}{}^{-}(R_\alpha)]=(2R_\alpha/\pi)^{1/2} \times J_{L_\alpha+1/2}[(k_\alpha^2-2W_\alpha(R_\alpha))^{1/2}R_\alpha/\hbar] \quad \text{at} \quad R_\alpha>R_{\alpha 0}(k_\alpha). \qquad (72)$$

The choice of (72) can be justified by the fact that in the heavy mass limit the functions $\chi_{L_\alpha}{}^{+}(R_\alpha)+\chi_{L_\alpha}{}^{-}(R_\alpha)$ as well as $J_{L_\alpha+1/2}\{[k_\alpha^2-2W_\alpha(R_\alpha)]^{1/2}R_\alpha/\hbar\}$ oscillate rapidly except in the vicinities of the stationary phase points where the argument is equal to the index. The left-hand side of (72) also has the necessary asymptotes both at $R_\alpha \to \infty$ and in the quasiclassical region if the argument is less than the index. By means of (71) and (72) it is possible in the expressions for the cross sections of Sec. III to carry out summation over the angular momenta in the same way as it was done in the model cases in the preceding section. We shall not reproduce here the relevant, rather cumbersome, although essentially simple, calculations. We shall only point out that the cross section can be expressed only in terms of the integrals over R_α and θ, the dependence on θ being defined by the behavior of the elastic scattering amplitudes in the initial and final channels contained in the integrands. These amplitudes are obtained in the expressions for the cross sections after summation (integration) over the angular momenta. At a given functional form of the cross sections which can be taken directly from experiment, these integrals are derived using the stationary phase method. The only quantity which requires the use of many-particle quantum-mechanical calculations is $\mathcal{V}(r_{i0}\ r_{f0})$, which, however, appears in the cross section only as the coefficient and does not depend on the heavy particle mass and therefore is not important in many cases where it is sufficient to use only relative probabilities.

Let us consider now the most important qualitative properties of cross sections. Here, in accordance with what has been said above, we can use the general results of the preceding section, substituting the squares of momenta k_α^2 by the quantity $p_\alpha^2 = k_\alpha^2 - 2W_\alpha$:

$$k_\alpha \to p_\alpha \equiv (k_\alpha^2 - 2W_\alpha)^{1/2}. \tag{73}$$

Here W_α is the value of $W_\alpha(R_\alpha)$ at the "reaction point" determined basically by the saddle point method in the corresponding integral. In what follows we shall consider W_α as additional empirical parameters characterizing the effective energy barriers.

As it follows from the results of Sec. IV, at the reaction distances removed far enough from the repulsive core of radius $R_{\alpha 0}$, the reaction products will scatter forward. On the other hand, at small reaction distances backward scattering will take place. It is natural to compare the former extreme situation to the so-called stripping reactions, and the latter to the so-called rebound reactions.[1] In order to consider further general characteristics of the cross sections it is necessary to take into account the energy conservation law, which we shall write in the form

$$Q + \tfrac{1}{2}p_f^2 + \epsilon_f = \tfrac{1}{2}p_i^2 + \epsilon_i; \qquad \epsilon_\alpha \equiv \mathcal{E}_{n\alpha} - U_\alpha(r_{\alpha 0}). \tag{74}$$

Here $\mathcal{E}_{n\alpha}$ is given by (36′) or (37′) and Q includes the change of electronic energy in the course of rearrangement of the system in the reaction region as well as the difference $W_f - W_i$ arising due to replacement of (73). The latter quantity is the difference of the potential barriers of elastic scattering for reagents and products. Usually it is small compared to the total value of Q. Now by means of (51) and (69) we can write the exponential factor in the expression for the cross section at the optimum angle as

$$\sigma(\theta = \theta_{\text{opt}}) \propto \exp\Big(-(\sin^2\eta)^{-1} \times \{[(p_i \cos\eta - p_f)^2/\hbar\omega_i] + [(p_i - p_f \cos\eta)^2/\hbar\omega_f]\}\Big). \tag{75}$$

Eliminating by means of (74) the final momentum p_f from (75) at a fixed scattering angle of products and reagents and at fixed states of internal motion, we can obtain an expression for $\sigma(\theta = \theta_{\text{opt}})$ as a function of the initial kinetic energy $\mathcal{E} = \frac{1}{2}k_i^2 = \frac{1}{2}p_i^2 + W_i$. The expression thus obtained has a characteristic maximum at a certain energy $\mathcal{E} = \mathcal{E}_{\text{res}}$, corresponding, according to (75), to the minimum value of $(p_i \cos\eta - p_f)^2$ and $(p_i - p_f \cos\eta)^2$. For stripping reactions the result obtained can be formulated as the principle of minimum transferred momenta $\hat{\mathfrak{q}}_\alpha$ during the reaction[19] (see also Ref. 20). In accordance with the principle of minimum transferred momenta, the cross section $\boldsymbol{\sigma}$ of the reaction under consideration at the fixed quantum numbers l_i, n_i and l_f, n_f has a maximum at the initial reaction energy and at the reaction angle for which each of the quantities assumes the minimum admissible value complying with the energy conservation law (74). This principle can be extended to the case of rebound reactions if it is required that the momenta transferred during the reaction should be minimum with respect to the motion along the combined quasiclassical trajectory of elastic scattering with certain optimum impact parameters. This suggestion about the optimum reaction trajectory being made up simply of two segments elastic scattering from in and out channel was actually made in Ref. 1. It can be justified, of course, only for the case of a reaction cross section much less than that of elastic scattering.

Let us examine, taking account of (74), the quantity figuring in the exponent in (75):

$$\begin{aligned}
&[(p_i \cos\eta - p_f)^2/\hbar\omega_i] + [(p_i - p_f \cos\eta)^2/\hbar\omega_f] \\
&\quad = \{\hbar^{-1}(\omega_i^{-1} + \omega_f^{-1})[p_i^2(1+\cos^2\eta) - 2p_i(\cos\eta) \\
&\qquad \times (p_i^2 - 2Q_{fi})] - (2/\hbar)Q_{fi}[\omega_i^{-1} + (\cos^2\eta/\omega_f)]\}; \\
&\qquad Q_{fi} = Q + \epsilon_f - \epsilon_i.
\end{aligned} \tag{76}$$

Let us calculate the derivative of (76) with respect to p_i. We shall obtain an equation, solving which with respect to p_i^2, we shall find the expressions for the resonance energy $\mathcal{E}_{\text{res}}$, i.e., the energy corresponding to the maximum effective cross section:

$$\begin{aligned}
\mathcal{E}_{\text{res}} &= W_i + \tfrac{1}{2}(p_{i\,\text{res}}^2) \\
&= W_i + (1+\cot^2\eta)Q_{fi} \quad \text{at} \quad Q_{fi} > 0 \\
&= W_i + (\cot^2\eta)\,|Q_{fi}| \quad \text{at} \quad Q_{fi} < 0.
\end{aligned} \tag{77}$$

Equations (77) show that the effective cross section maximum is reached at the value of energy higher than the threshold value by the quantity $(\cot^2\eta)\,|Q_{fi}|$. This is a typical many-particle effect. After substitution of $p_{i\,\mathrm{res}}$ into (75), by means of (76) we obtain:

$$\sigma(\theta=\theta_{\mathrm{opt}})\,|_{p_i=p_{i\,\mathrm{res}}}\propto\exp(-2Q_{fi}/\hbar\omega_f)\quad\text{at}\quad Q_{fi}>0,$$
$$\propto\exp(-2\,|Q_{fi}|/\hbar\omega_i)\quad\text{at}\quad Q_{fi}<0. \tag{78}$$

From (78) it is possible to draw some interesting conclusions regarding the ratio of initial and final quantum states that would be optimum for the reaction. The most favorable would be the values of the quantum numbers corresponding to minimum $|Q_{fi}|$. In particular, in the case when the energy range nearest to the reaction threshold is of interest, we can draw the following conclusions:

(1) For an exothermic reaction ($Q<0$) the conditions most favorable for the reaction are those when the initial bound state is unexcited and the final bound state is excited, so that two consecutive optimum values of ϵ_f—$\epsilon_f(n_f^{\mathrm{opt}})$, $\epsilon_f(n_f^{\mathrm{opt}}+1)$—satisfy the condition

$$\epsilon_f(n_f^{\mathrm{opt}})\leq|Q|\leq\epsilon_f(n_f^{\mathrm{opt}}+1). \tag{79}$$

(2) In the case of an endothermic reaction ($Q>0$) the most favorable conditions are those when the final bound state is excited, so that two consecutive optimum values of ϵ_i: $\epsilon_i(n_i^{\mathrm{opt}})$, $\epsilon_i(n_i^{\mathrm{opt}}+1)$ satisfy the condition

$$\epsilon_i(n_i^{\mathrm{opt}})<Q<\epsilon_i(n_i^{\mathrm{opt}}+1). \tag{79'}$$

So far we have ignored the restrictions of applicability of the expressions for the cross sections of the form (75) at $q_\alpha^2<\hbar\omega_\alpha$ due to the decrease of the cross section at small q_α^2 mentioned in Sec. IV. In accordance with (51′), in the range $q_\alpha^2<\hbar\omega_\alpha$ the reaction cross section should decrease significantly the larger l_α is, provided there are no long range forces at play, such as those of Coulombic or charge-dipole attraction. The threshold decrease of the cross section extends from zero energies to those comparable with a vibration quantum. These observations are of particular importance in considering the values of l_α that are optimum for the occurrence of the reaction at other fixed quantum numbers. As a result, along with the optimum quantum numbers of vibrations n_α, there arise the optimum quantum numbers of angular momenta l_α. At sufficiently large l_α one should use the wave functions and expressions for ϵ_α corresponding to the spherical oscillator (37′). It should be pointed out that the presence of optimum quantum numbers of vibrations and rotations was revealed in investigation of reactions in molecular beams.

The above considerations refer to the positions of the cross section maxima treated as the functions of the square root of the kinetic energy at given quantum numbers of initial and final states. The half-widths of these maxima Γ_{fi} at the point $p_i=p_{i\,\mathrm{res}}$ because of the uncertainty of atomic momenta, there being no absolutely rigid initial and final bound states, and defined by the value of the square root of the second derivative of (76) with respect to p_i at $p_i=p_{i\,\mathrm{res}}$ are equal to

$$\Gamma_{fi}=[\hbar\omega_i\omega_f/(\omega_i+\omega_f)]^{1/2}\sin^2\eta. \tag{80}$$

Thus the values of Γ_{fi} depend on the masses and the corresponding kinetic energy ranges are less than the vibration quantum value.

In conclusion, one more remark should be made. It follows from the consideration of the equations for the cross sections that in the case of rebound reactions the molecules formed should be mostly polarized perpendicular to the directon of the momentum.

VI. COMPARISON WITH EXPERIMENT

The general conclusions obtained above which follow from the existence of specific many-particle quantum effects may be compared with experiment in two ways. The first way is to compare the conclusions of the theory with the general regularities of more or less monoenergetic (with respect to kinetic energy) experiments. The second way is to compare the theory with the results of usual thermal chemical measurements.

To widen, especially in the second case, the possibilities of comparison with experiment, let us first consider briefly the distinctions that may arise when R_k are not monatomic, but multiatomic fragments. First of all, the kinematics will change: we shall have a larger set of radius vectors connecting the heavy particles, and a reasonable choice of "external" and "internal" coordinates of the form $\mathbf{R}_\alpha$, $\mathbf{r}_\alpha$ will require further physical treatment. The simplest limiting case is that when the mass of the multiatomic fragment R_3 can be assumed to be infinite, i.e., $m_3\gg m_1$, m_2 and the fragments R_1 and R_2 remain simple. Then it would be reasonable to choose the vectors $\mathbf{R}_\alpha$ as the distances from the positions of the centers of mass of simpler fragments R_1, R_2 to the position of the outer atom of R_3, participating in the bond formation. In this limiting case we may retain the definition of the kinematic angle η adopted above. Another important difference arises in the multiatomic case owing to increase in the number of the degrees of freedom, part of which can be classical, i.e., corresponding to the almost continuous change of admissible energy values. These latter degrees of freedom include, e.g., vibrations along loose bonds.

In the experiments carried out so far, both monoenergetic and thermal, there is always a set of rotation states in the initial states which usually corresponds to a certain equilibrium distribution. According to the results obtained, the reaction cross section averaged over rotations, at given values of the other quantum numbers, should show a characteristic dependence on kinetic energy (Fig. 1) with initial increase defined by the half-width (80) and further relatively slow drop due to addition of consecutively decreasing contributions of the rotation states. According to what has been said above about the threshold behavior, the total width of these over-all maxima should be less than a vibration quantum. This behavior of the reaction cross sections with a characteristic energy maximum was most distinctly revealed in the treatment of reactions with hot tritium atoms[4] and in ion and hydrogen atoms beams.[21]

The results of the preceding section also illuminate the basic facts known from the studies on the substitution reactions in molecular beams and summarized in Ref. 1. In particular, an insight is gained into the phenomenon of the preferential energy release as excitations of the internal degrees of freedom, a process which was observed also in usual exothermic reactions as well as in ion–molecular reactions. For endothermic reactions the reaction cross section at given total energy, according to the results of Sec. V, should be greater for reagents with excited internal degrees of freedom. Thus the products of exothermic reactions should enter into subsequent endothermic reactions more quickly at the moment of their formation in the excited state before the relaxation of the excitations of internal degrees of freedom than the molecules with the same kinetic energy at the equilibrium distribution tail.

For a general comparison of the conclusions of the theory with the results of the studies of "thermal" reactions, it is necessary to perform a complete averaging of cross sections over the equilibrium distribution. To the very first approximation, assuming $(\Gamma_{fi})^2 < kT$ and retaining in the total effective cross section only the contributions of two most intensive transition groups with the lowest energy value, by means of (79), we can obtain an expression for the reaction rate constant:

$$k(T) = A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/kT), \quad (81)$$

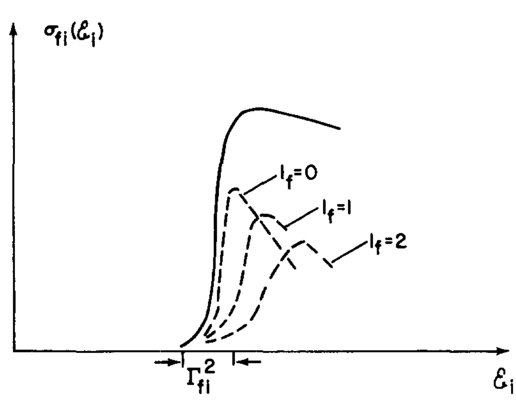

FIG. 1. Scheme of the dependence of the reaction cross section $\sigma(\mathcal{E}_i)$ on initial energy $\mathcal{E}_i$ at different quantum numbers of angular momentum l_f. The solid line is the envelope of the sum of cross sections with different l_f.

TABLE I. Calculation of the activation energies of Form (84) for hydrogen isotope reactions.

Reaction	Activation energy (kcal/mole)		Error (approx)
	Experiment[a]	Calculation	
$H+pH_2$	8.8	9.1	3%
$D+pD_2$	7.6	7.4	3%
$D+H_2$	9.1	8.8	3%
$H+D_2$	7.3	7.0	4%

[a] References 22–25.

where for an exothermic reaction,

$$E_1 = W_i + (|Q| - n_f^{\text{opt}}\hbar\omega_f)\tan^2\eta,$$
$$E_2 = W_i + [(n_f^{\text{opt}}+1)\hbar\omega_f - |Q|](1/\sin^2\eta), \quad (82)$$

and for an endothermic reaction,

$$E_1 = W_i + (Q - n_i^{\text{opt}}\hbar\omega_i)(1/\sin^2\eta) + n_i^{\text{opt}}\hbar\omega_i,$$
$$E_2 = W_i + [(n_i^{\text{opt}}+1)\hbar\omega_i - Q]\tan^2\eta + (n_i^{\text{opt}}+1)\hbar\omega_i. \quad (83)$$

In (82) and (83) we take the energy levels of a spherical oscillator (37′). In a sufficiently narrow temperature range expression, Eq. (81) can be approximately reduced to the Arrhenius equation with an effective activation energy E_a:

$$E_a = -\frac{d\ln k(T)}{d(1/kT)} = \frac{A_1E_1\exp(-E_1/kT) + A_2E_2\exp(-E_2/kT)}{A_1\exp(-E_1/kT) + A_2\exp(-E_2/kT)} = (1-\lambda)E_1 + \lambda E_2. \quad (84)$$

The parameter λ $(0 \leq \lambda \leq 1)$, which depends but slightly on T, takes account of the details of the cross section ratios for two transition groups. Thus, for an endothermic reaction we have

$$E_a = W_i + \left[\left(\lambda\frac{1+\cos^2\eta}{\sin^2\eta} - \cot^2\eta\right)n_i^{\text{opt}} + \frac{\lambda}{\sin^2\eta}\right]\hbar\omega_i - \left(\lambda\frac{1+\cos^2\eta}{\sin^2\eta} - \cot^2\eta\right)Q + Q. \quad (85)$$

and for an exothermic reaction,

$$E_a = W_i + \left[\left(\lambda\frac{1+\cos^2\eta}{\sin^2\eta} - \cot^2\eta\right)n_f^{\text{opt}} + \frac{\lambda}{\sin^2\eta}\right]\hbar\omega_f - \left(\lambda\frac{1+\cos^2\eta}{\sin^2\eta} - \cot^2\eta\right)|Q|. \quad (86)$$

It would be of interest to compare the above equations with the data of the measurements (accurate to

TABLE II. Comparison with experiment[28] of the calculated activation energies for $H+X_2$ at $W_i=1.38$ kcal/mole and $\lambda=0$.

Reaction	Thermal effect (kcal/mole)	Activation energy (kcal) Experiment (mean value)	Activation energy (kcal) Calculated value
$H+F_2$	−98	2.4	1.74
$H+Cl_2$	−44	1.8	1.42
$H+Br_2$	−42	0.9	1.38
$H+J_2$	−35	0.9	1.35

5%)[20–25] of the activation energies of the hydrogen isotopes reactions, listed in Table I. Using the least squares method and taking into account the measured values of the vibration quanta, we obtain the optimum parameter values: $W_i=W_f=3.2$ kcal/mole and $\lambda=0.35$. Even if this calculation for hydrogen reactions is rather conditional, it is significant that the general isotopic behavior of the activation energy, hardly explainable within the framework of conventional concepts, proves to be correct. Evidently, this behavior should change with increasing temperature, only when an approximate account of the contribution of two channels no longer suffices. We think that this fact accounts for the results of the measurements at more elevated temperatures.[26] It should be emphasized that the main contribution to the activation energy in the model under consideration is made by the effect of the many-particle quantum nature of the phenomenon itself, rather than by the repulsion related to the potentials W_α, as is the case in the classical reaction models. Recent experiments on the substitution reactions with a light hydrogen isotope μ^+ mesonium[27] showed an isotopic decrease of the activation energy which agrees with the deduced equations.

It is interesting to note that Eqs. (85) and (86) explain the empirical Polanyi rule for the activation energies and also the observed deviations from it for the reactions with participation of the lightest fragments of the homological series. According to this rule, the activation energy for the homological series reactions varies as a linear function of the thermal effect with a positive coefficient of proportionality. Some examples of the Polanyi rule and of the deviations from it for the lightest fragments were theoretically calculated in Ref. 12 using the given scheme.

Further, it follows from Eqs. (85) and (86) that for large masses of the fragment transferred $m_1 \gg m_2$, m_3 we must have the Polanyi coefficient which will be a small negative quantity for exothermic reactions and a quantity somewhat larger than unity for endothermic reactions. It proves that such general behavior of the activation energies is actually observed in the case of $H+X_2$ reactions, where X is the halogen atom (see Table II).

Special consideration should be given to reactions between ions as well as between ions and dipole molecules (in the initial state for exothermic and in the final state for endothermic reactions) and also for other reactions with slowly diminishing potentials $U_\alpha(r_\alpha)$. Since in this case the formulas of the form (49) are valid and, accordingly, the threshold limitations mentioned in Sec. V are removed, the optimum kinetic energy values in the sense of 6 "slip down" to the energy threshold. As the result, the activation energy should decrease substantially and approach W_i.

VII. CONCLUSIONS

In this paper, equations are proposed for calculation of the cross sections of the simplest substitution reactions, based on information on elastic scattering and bound states. The approximation used may be justified within the framework of the general quantum-mechanical theory of scattering.[14,15] At the same time it is a generalization of a two-level approximation, which has long been used for description of atom–atom collisions.[29] We have introduced the effective potentials $W_\alpha(R_\alpha)$, $\mathcal{V}(r_i, r_f)$ for description of elastic scattering and transition between the channels, respectively. The specificity of the problem being considered lies in the fact that here the appearance of the above-mentioned potentials is due to the presence of electrons. Owing to the smallness of the ratio of the electron mass to atomic masses, these potentials can be roughly considered to be local and energy independent. In calculations of the reaction cross sections a special multidimensional WKB approximation was developed taking into account the elastic scattering and transition between the channels. For simplicity, certain additional assumptions regarding the form of effective potentials were made. However, as is clear from the consideration of the method of transition to the heavy mass limit in Secs. III–V, the main results obtained should depend slightly on these assumptions.

In terms of the approach used it is possible to give a natural explanation of the basic qualitative peculiarities of the energetic and angular dependences of the cross sections of the simplest substitution reactions, including the correlation between the cross section, angular distribution and reaction type. Some of the results mentioned have been obtained by a different approach in previous publications.[30]

The peculiarities mentioned at the end of Sec. VI arise in reactions involving ions and also in reactions with long-range interaction forces in ionic molecules, where the activation energy is much lower. In view of these facts, we think that it would be reasonable to divide the reactions which do not involve formation of collision complexes into our extreme classes rather than into two: (1) involving formation of polar bonds such as ionic (including the reactions of the so called harpoon type,[1] (2) stripping reactions proper, (3) rebound

TABLE III. Classification of direct substitution reactions.

Reaction type	Preferential scattering of products		Optimum energy distribution according to degrees of freedom		Contribution of many-particle quantum effects to activation energy
	Forward	Backward	Internal degrees	Kinetic energy of translational motion	
1. With contribution of ionic bonds	+		+		−
2. Stripping reactions	+		+		+
3. Rebound reactions		+	+		+
4. Tunnel reactions		+		+	−

reactions proper, and an additional class, (4) tunnel reactions. In the last-mentioned type of reactions we have an optimum situation when the maximum energy accumulates on translational degrees of freedom. Each of the reaction classes mentioned is characterized in a special manner, apart from direction, by the peculiarities of the optimum distribution according to the degree of freedom of the energy released (consumed) during the reaction (see Table III). Along with these extreme types, there can also occur, of course, intermediate cases, where the influence and concrete form of the potentials W_α should be dealt with in more detail.

By means of the expressions for the cross sections obtained, a statistical averaging was carried out to the first approximation, involving calculation of the general form of the rate constants of chemical reactions. It is very promising that these procedures enabled us to explain in a natural way a number of experimentally found relations such as the Polanyi rule and, particularly, the deviations from it.

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