$$W(t)=\sum_{k,\mu}|C_{k,\mu}(t)|^2=\gamma|V_{n\rho_0}|^2\frac{1}{(\varepsilon_{p_0}+|I_0|-\omega)^2+(\Gamma-\Gamma_0)^2/4}$$
$$\times\left\{\frac{1}{\Gamma}(1-e^{-\Gamma t})+\frac{1}{\Gamma_0}(1-e^{-\Gamma_0 t})-\frac{(\Gamma+\Gamma_0)K}{(\varepsilon_{p_0}+|I_0|-\omega)^2+(\Gamma+\Gamma_0)^2/4}\right\},\quad (A.2)$$

where

$$K=1-\exp(-{}^1/_2(\Gamma+\Gamma_0)t)\,[\cos(\varepsilon_{p_0}+|I_0|-\omega)t$$
$$-2(\varepsilon_{p_0}+|I_0|-\omega)\sin(\varepsilon_{p_0}+|I_0|-\omega)t].$$

[1]L. I. Gudzenko, L. V. Gurvich, V. S. Dubov, and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. **73**, 2067 (1977) [Sov. Phys. JETP **46**, 1082 (1977)].

[2]R. Z. Vitlina, A. V. Chaplik, and M. V. Éntin, Zh. Eksp. Teor. Fiz. **67**, 1667 (1974) [Sov. Phys. JETP **40**, 829 (1974)].

[3]T. A. Vartanyan and S. G. Przhibel'skiĭ, Zh. Eksp. Teor. Fiz. **74**, 1579 (1978) [Sov. Phys. JETP **47**, 824 (1978)].

[4]V. I. Goldanskii, F. I. Dalidchik, and G. K. Ivanov, Appl. Phys. **5**, 81 (1974).

[5]S. I. Vinitskiĭ, L. I. Ponomarev, I. V. Puzynin, T. P. Puzynina, L. N. Somov, and M. P. Faĭfman, JINR Preprint R4-10929, 1977.

[6]W. Heitler, The quantum theory of radiation, Oxford, 1954 (Russ. Transl. IIL, 1956).

[7]É. A. Vesman, Pis'ma v Zh. Eksp. Teor. Fiz. **5**, 113 (1967) [JETP Lett. **5**, 91 (1967)].

Translated by E. Brunner

Quasiclassical theory of direct chemical reactions in rapid collisions

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(Submitted 14 March 1979)
Zh. Eksp. Teor. Fiz. 77, 872–883 (September 1979)

The amplitude of the rearrangement reactions that accompany fast molecule collisions is analyzed within the framework of the eikonal approximation. Calculation of the eikonal integral by the stationary-phase method establishes the presence of different process mechanisms, each connected with a region of scattering angles and energies in which the mechanism makes the decisive contribution to the cross section. For the differential cross section in the vicinity of the principal directions connected with these mechanisms, simple analytic formulas are obtained and connect the angular distribution with the parameters of the binary potentials between the atoms. The rate constants of the chemical reactions are estimated on the basis of the obtained approximate expressions.

PACS numbers: 82.20.Hf, 82.30.Eh

The development of effective analytic methods for the estimate of the cross sections, and also of the constants of chemical reactions in the energy interval from several electron volts and upwards is of great interest for a large number of gas dynamic problems at high temperatures.

It is known that at such energies the dominant mechanism is in many cases the mechanism of direct reactions,[1] which means both the absence of an intermediate complex and a decrease of the role of the nonadiabatic transitions between the potential surfaces. These reactions were investigated most consistently in the impulse approximation[2] under the conditions.

$$\tau\omega\ll 1,\quad \mathcal{F}\ll\rho_0,\qquad (1)$$

where ω is the characteristic frequency of the vibrations of the nuclei, τ is the collision time, $\mathcal{F}$ is the amplitude of the pair scattering, and ρ_0 is the average distance between atoms. In addition, an additive model of interaction potentials was used. It must be stated that the second condition of (1) is too stringent, as is incidentally also the first.

Much more accurate is the eikonal approximation developed for the rearrangement reactions in our preceding papers.[3-5] It is not connected with the second condition of (1) and makes it possible to relax the first somewhat. The eikonal formulas take fuller account of the interaction between the particles and make it possible, as we shall show below, to describe correctly within the framework of a single expression the "stripping," "pickup," and "knock-out" mechanisms. In the present paper we obtain from the eikonal expression a general formula of quasiclassical character for the amplitude of the stripping and pickup reactions, which yields the contribution to the small-angle scattering. This formula at lower energies than in the impulse approximation. Next, for all three mechanisms at higher energies, we obtain simple analytic formulas for the scattering amplitudes, applicable for mass calculations of the cross sections and of the rate constants of reactions at high temperatures. We obtain for the rate constants of the reactions analytic expressions that depend on the principal parameters of the colliding partners.

0038-5646/79/090440-07$02.40

§1. GENERAL EIKONAL FORMULA FOR THE REACTION AMPLITUDE, AND THE STRIPPING, PICKUP, AND KNOCK-OUT MECHANISMS

We consider for the sake of argument the process

$$1+(2.\ 3)_n \to 2+(1.\ 3)_m, \tag{2}$$

for which a general eikonal expression was obtained for the scattering amplitude

$$f_{mn}(\mathbf{k}_i, \mathbf{k}_f) = \frac{\mu_1}{4\pi\hbar^2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \varphi_m^*(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)\left[V_2 \exp\left(\frac{i\Delta S_i}{\hbar}\right) + V_1 \exp\left(\frac{i\Delta S_f}{\hbar}\right)\right] \tag{3}$$

Here μ_1 is the reduced mass of the particle 1 and of the (2, 3) pair, $\mathbf{r}_{1,2}$ are the radius vectors of particles 1 and 2 relative to particle 3, $\varphi_{n,m}$ are the wave functions of the bound states, and $V_{1,2}$ are the potentials of the interaction in the entrance and exit channels. For the increments $\Delta S_{i,f}$ of the action in the input and exit channels we have the expressions

$$\Delta S_{i,f} = \varkappa_1\mathbf{r}_1 + \varkappa_2\mathbf{r}_2 + \delta_{i,f},$$
$$\delta_i = -\int_0^\infty V_1(\boldsymbol{\rho}_1 - \mathbf{v}_i t, \boldsymbol{\rho}_2)\, dt, \quad \delta_f = -\int_0^\infty V_2(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2 + \mathbf{v}_f t)\, dt. \tag{4}$$

In (4), $\varkappa_{1,2}$ are the momenta transferred to particles 1 and 2 in the laboratory frame ($\varkappa_1 = \mathbf{k}_i - \Delta m_1/M_{13}, \varkappa_2 = \mathbf{k}_f, \mathbf{k}_i, \mathbf{k}_f\Delta$ are the momenta of particles 1, 2 and the pair (1, 3) in the laboratory frame), $\boldsymbol{\rho}_{1,2}$ are the Jacobi coordinates of the particles, $\mathbf{v}_i = \mathbf{k}_i/m_1, \mathbf{v}_f = \mathbf{k}_f/m_2 - \Delta/M_{13}$ are the relative velocities of the particles 1 and 2, respectively.

It was shown in Ref. 5 that expression (3) describes all three direct-reaction mechanisms (stripping, pickup, knock-out) that manifest themselves distinctly in the angular distribution, depending on the ratio between the coupling constants $\gamma_n = (2m_{23}|E_n|)^{1/2}/\hbar, \gamma_m = (2m_{13}|E_m|)^{1/2}/\hbar$ of the pairs (2, 3) and (1, 3). Choosing the wave functions $\varphi_{n,m}$ in the form (we take into account for simplicity only the spherically symmetrical states)

$$\varphi_{n,m} = Q_{n,m}(r)\exp(-\gamma_{n,m}r) \tag{5}$$

and introducing the arguments of the exponentials in the classical action, we consider complex actions defined by the condition (for the stripping and pickup mechanisms)

$$\Delta S_{i,f}^{\text{eff}} = \Delta S_{i,f} + i\hbar\gamma_n r_2 + i\hbar\gamma_m r_1. \tag{6}$$

These complex actions must be considered in order to introduce complex trajectories for the nonclassical reaction mechanisms. As will be shown later on, for the knock-out mechanism it is useful to introduce the variables $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and express the classical actions in the form

$$\Delta S_{i,f}^{\text{eff}} = (\varkappa_1 + \varkappa_2)\mathbf{R} + {}^1/_2(\varkappa_1 - \varkappa_2)\mathbf{r} + i\hbar\gamma_m|\mathbf{R} + {}^1/_2\mathbf{r}| + i\hbar\gamma_n|\mathbf{R} - {}^1/_2\mathbf{r}|. \tag{7}$$

We consider now those simplifications that can be introduced in (3) when it comes to describing the angular distribution near the eikonal directions corresponding to the three different reaction mechanisms. The conclusions presented below follow from a simple analysis of the values of the classical action (6) and (7).

a) At $\gamma_n \ll \gamma_m$ the eikonal direction is determined obviously by the condition

$$\varkappa_2 \approx 0 \quad \left(\mathbf{k}_f \approx 0,\ \mathbf{k}_i \approx \Delta,\ \varkappa_1 \approx \frac{m_3}{M_{13}}\mathbf{k}_i\right) \tag{8}$$

and makes it possible to introduce the following simplifying assumptions (we choose the additive model of the interaction and we assume the pair potentials, for simplicity, to be spherically symmetrical):

$$V_1 \approx V_{13}(r_1), \quad V_2 \approx V_{12}(r_2) + V_{32}(r_2), \quad r_1 \ll r_2. \tag{9}$$

This is the nonclassical stripping mechanism, wherein particle 1 "tears out" the particle 3, and the pair (1, 3) travels approximately forward, while particle 2, located at a large distance from 3, plays the role of the "nonparticipating observer."

b) On the contrary, at $\gamma_n \gg \gamma_m$ the maximum of the angular distribution corresponds to the conditions

$$\varkappa_1 \approx 0, \quad \Delta \approx \frac{M_{13}}{m_1}\mathbf{k}_i, \quad \varkappa_2 = -\mathbf{k}_f \approx \frac{m_3}{m_1}\mathbf{k}_i \tag{10}$$

and makes it possible to introduce the simplifications

$$V_1 \approx V_{13}(r_1) + V_{12}(r_1), \quad V_2 \approx V_{23}(r_2), \quad r_1 \gg r_2. \tag{11}$$

These conditions characterize the pickup mechanism, wherein the particle 1 "pushes out" 3 approximately forward and, being scattered from particle 2 in the same direction, forms the pair (1, 3); the particle 2 then moves approximately backwards. All this takes place at a large distance between particle 1 and the pair (2, 3). These two mechanisms make separate contributions which are predominantly directed forwards.

c) At $\gamma_n \approx \gamma_m$, besides the foregoing, there is another effective mechanism, knock-out, characterized by the conditions

$$\varkappa_1 + \varkappa_2 \approx 0, \quad \Delta \approx 0, \quad \mathbf{k}_i \approx \mathbf{k}_f \tag{12}$$

and by the simplifying assumptions

$$V_1 \approx V_2 \approx V_{12}(r), \quad r \ll R. \tag{13}$$

Within the framework of this mechanism, particle 1 "knocks out" 2 by frontal collision forward, and the produced pair (1, 3) travels predominantly into the rear hemisphere. It is clear that at an arbitrary ratio of γ_n and γ_m it is necessary to take into account the contributions of all three mechanisms. We shall now use the simplifying assumptions (9), (11), and (13) to calculate by the stationary-phase method the angular distribution near the eikonal directions characterized by conditions (8), (10), and (12).

§2. CALCULATION OF THE ANGULAR DISTRIBUTION NEAR THE EIKONAL DIRECTIONS BY THE STATIONARY-PHASE METHOD

1. In the investigation of the six-dimensional integral (2) as $\hbar \to 0$ by the stationary-phase method[6] we must first find the stationary points $\mathbf{r}_1^0$ and $\mathbf{r}_2^0$, which are obtained from the conditions (for the stripping and pickup reactions)

$$\varkappa_1 = \int_0^\infty \nabla_{\mathbf{r}_1} V_1(|\mathbf{r}_1 - \mathbf{v}_i t|)\, dt - i\hbar\gamma_m \frac{\mathbf{r}_1}{r_1},$$

$$\varkappa_2=\int_0^\infty \nabla_{\mathbf{r}_2} V_2(|\mathbf{r}_f+\mathbf{v}_f t|)\,dt - i\hbar\gamma_n \frac{\mathbf{r}_2}{r_2}. \tag{14}$$

After subtracting the imaginary increments which are small as $\hbar \to 0$, Eqs. (14) acquire a simple physical meaning, namely that the increments of the momenta of particles 1 and 2 during the collision time are equal to the corresponding momenta of the forces. We note that the separation of the variables in Eqs. (14) takes place within the framework of the approximations (9) and (11) for the potentials, which we in fact employ. It is easy to verify that the stationarity configurations are planar ($z_1^0=z_2^0=0$). To calculate $x_1^0 y_1^0$ and $x_2^0 y_2^0$ we choose the coordinate system in the following form: we direct the x axis along the bisector of the angle $\sphericalangle(\mathbf{k}_i, \Delta)\equiv\theta$, and the y axis antiparallel to the vector $\mathbf{k}_f$. Retaining in the numerators only the terms proportional to θ, we obtain ultimately

$$\frac{2m_3}{m_1+m_3}\mathscr{E}=V_1(x_1^0), \quad y_1^0=\frac{\theta}{I_1}\left[-\frac{2m_1}{m_1+m_3}\mathscr{E}-\frac{x_1^0 I_1}{2}\right]; \tag{15}$$

$$\frac{2\zeta m_1}{m_{23}}\mathscr{E}+i\hbar\frac{k_i\gamma_n}{m_{23}}=V_2(x_2^0), \tag{16}$$

$$y_2^0=\frac{\theta}{I_2}\left[\frac{2m_3+m_2}{m_3}x_2^0 I_2-\frac{2m_1\mathscr{E}}{m_{23}}-\frac{2m_3+m_2}{2m_3}V_2(x_2^0)\right],$$

where

$$\zeta=\begin{cases} m_3/m_1, & \varkappa_1\approx 0 \\ 0, & \varkappa_2\approx 0 \end{cases}; \quad \mathscr{E}=\frac{k_i^2}{2m_1},$$

$$I_1=\int_{|x_1^0|}^\infty V_1'(z)\frac{dz}{z}, \quad I_2=\int_{x_2^0}^\infty V_2'(z)\frac{dz}{z}. \tag{17}$$

We discuss now Eqs. (15) and (16). The first equation of (15) obviously yields a finite negative value x_1^0 determined by the short-range part of the potential V_{13}. The first equation of (16) for the stripping mechanism ($\varkappa_2\approx 0$) leads to an infinite value of x_3^0 if the imaginary increment $\propto\hbar$ is neglected, corresponding to degeneracy of the asymptotic form. From the physical point of view this means that the stripping mechanism has a nonclassical character, i.e., it is realized on a complex trajectory determined with account taken of the imaginary increment $\propto\hbar$, in analogy with the case of elastic scattering through small angles.[7] Neglecting the contribution of the remaining complex solutions x_2^0, we confine ourselves only to that value of x_2^0 which has the smallest imaginary part and goes over as $\hbar\to 0$ into the classical solution. For the classical pickup mechanism ($\zeta=m_3/m_1$) we can neglect the imaginary increment. If x_2^0 is complex, I_2 is taken to mean a contour integral. In the calculation of y_2^0 we can omit the imaginary increment to x_2^0. We now represent the initial expression (3) in the form

$$f_{mn}(\mathbf{k}_i,\mathbf{k}_f)=\frac{\mu_1}{4\pi\hbar^2}\iint d\mathbf{r}_1\,d\mathbf{r}_2\,\varphi_m^*(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)\exp\left(\frac{i}{\hbar}\Delta S_+\right)$$

$$\times\left[V_2\exp\left(\frac{i}{\hbar}\Delta S_-\right)+V_1\exp\left(-\frac{i}{\hbar}\Delta S_-\right)\right], \tag{18}$$

$$\Delta S_\pm={}^1/_2(\Delta S_i\pm\Delta S_f) \tag{19}$$

and assume that the stationary-phase point is determined by the total increment of the action on the trajectory ($\nabla_{\mathbf{r}_1}\Delta S_+=0, \nabla_{\mathbf{r}_2}\Delta S_+=0$). It is obvious then that within the framework of our assumptions concerning the potentials the equations for the stationary point coincide with the previous equations (14). What we seek here essentially is a "true" eikonal trajectory consisting of two branches. One is specified by the initial momenta $\mathbf{k}_i n$ and final coordinates $\mathbf{r}_1^0\mathbf{r}_2^0$, and the other by initial coordinates $\mathbf{r}_1^0\mathbf{r}_2^0$ and final momenta $\mathbf{k}_f m$. The presence of two potentials V_1 and V_2 in different channels leads to a natural separation of the total trajectory at the point $\mathbf{r}_1^0\mathbf{r}_2^0$ into two branches (in analogy with the "impact-parameter plane" in the excitation problem). It is easy to verify that under our assumptions concerning the potentials, we have the following equations for the determinants:

$$D_+(\mathbf{r}_1^0,\mathbf{r}_2^0)=D_i(\mathbf{r}_1^0)D_f(\mathbf{r}_2^0), \tag{20}$$

$$D_+=\left|\frac{\partial^2\Delta S_+}{\partial(\mathbf{r}_1^0,\mathbf{r}_2^0)\partial(\mathbf{r}_1^0,\mathbf{r}_2^0)}\right|, \quad D_j(r_j^0)=\left|\frac{\partial^2\Delta S_j}{\partial\mathbf{r}_j^0\partial\mathbf{r}_j^0}\right|.$$

Using (15) and (16), we obtain next after a number of algebraic transformations, which will not be given here,

$$D_i=-\int_0^\infty V_i''(x_i^0-v_i t)\,dt\left[\int_0^\infty V'(x_i^0-v_i t)\frac{dt}{x_i^0-v_i t}\right]^2, \tag{21}$$

$$D_f=-\int_0^\infty V_2''(x_2^0+v_f t)\,dt\left[\int_0^\infty V_2'(x_2^0+v_f t)\frac{dt}{x_2^0+v_f t}\right]^2. \tag{22}$$

As seen from (22), $D_f\neq 0 (x_2^0\neq\infty)$ for the stripping mechanism only in the presence of an imaginary increment in the first equation of (16), i.e., we have a nondegenerate case for which the standard stationary-phase method equation is valid.[6] The use of this equation yields ultimately

$$f_{mn}(\mathbf{k}_f,\mathbf{k}_i)=\frac{\mu_1}{4\pi\hbar^2}(2\pi\hbar)^3\varphi_n(\mathbf{r}_2^0)\varphi_m^*(\mathbf{r}_1^0)D_+^{-1/2}$$

$$\times\left\{V_2(\mathbf{r}_2^0)\exp\left\{\frac{i}{\hbar}\Delta S_i(\mathbf{r}_1^0,\mathbf{r}_2^0)\right\}+V_1(\mathbf{r}_1^0)\exp\left\{\frac{i}{\hbar}\Delta S_f(\mathbf{r}_1^0,\mathbf{r}_2^0)\right\}\right\}. \tag{23}$$

Equations (15), (16), (21), and (22) make it thus possible, by using fundamentally simple calculations, to determine the small-angle angular distribution, with account taken of the stripping and pickup mechanisms. We consider now the question of obtaining a quasiclassical formula that describes the angular distribution of the produced (1, 3) pair in the rear half-plane, within the framework of the knock-out mechanism. In this case we make the change of variables $r_1, r_2 \to r, R$ and use the classical actions (7). Taking the approximation (13) into account, and neglecting also the phases of ΔS_-, we have for the knock-out amplitude an expression that is obtained when the integral with respect to r is evaluated by the stationary-phase method:

$$f_{mn}(\mathbf{k}_f,\mathbf{k}_i)=\frac{\mu_1}{m_{12}}\bar{f}(E,\vartheta)J(E,\vartheta). \tag{24}$$

Here $\bar{f}$ is the amplitude of the elastic predominantly backward scattering of particle 1 by particle 2, calculated by applying the stationary-phase method to the expression

$$f(E,\vartheta)=\frac{m_{12}}{2\pi\hbar^2}\int d\mathbf{r}\,V_{12}(\mathbf{r})\exp\left[\frac{i}{\hbar}\left\{\frac{\varkappa_1+\varkappa_2}{2}\mathbf{r}\right.\right.$$

$$\left.\left.-\frac{1}{2}\int_0^\infty V_{12}(\mathbf{r}-\mathbf{v}_i t)\,dt-\frac{1}{2}\int_0^\infty V_{12}(\mathbf{r}+\mathbf{v}_f t)\,dt\right\}\right]. \tag{25}$$

The stationary-phase point $\mathbf{r}_0(\vartheta, E)=(x_0, 0, 0)$ is obtained from the equation

$$\varkappa_1-\varkappa_2=\nabla_{\mathbf{r}}\left[\int_0^\infty V_{12}(\mathbf{r}-\mathbf{v}_i t)\,dt+\int_0^\infty V_{12}(\mathbf{r}+\mathbf{v}_f t)\,dt\right], \tag{26}$$

which determines the function $x_0(\vartheta, E)$, $\vartheta = \pi - \measuredangle(\mathbf{k}_i, \mathbf{k}_f)$. In the solution of (26) one uses, as is customary, a coordinate system with a y axis perpendicular to the plane of the vectors $\mathbf{k}_i$ and $\mathbf{k}_f$, a z axis directed along the bisector of the angle between the vectors $\mathbf{k}_i$ and $\mathbf{k}_f$, and an x axis directed antiparallel to the vector Δ.[7,8] The quantity $J(E, \vartheta)$ is defined by

$$J = \int d\mathbf{R} \exp\left[\frac{i}{\hbar}(\varkappa_1+\varkappa_2)\mathbf{R}\right] \varphi_m\left(\mathbf{R}+\frac{\mathbf{r}_0}{2}\right)\varphi_n\left(\mathbf{R}-\frac{\mathbf{r}_0}{2}\right). \tag{27}$$

By specifying the functions $V_{12}(\mathbf{r})$, $\varphi_{n,m}$ we can calculate the amplitude of the rearrangement reaction that proceeds via the knock-out mechanism.

§3. SIMPLIFIED ANALYTIC FORMULAS FOR THE REARRANGEMENT AMPLITUDE IN THE HIGH-ENERGY LIMIT

We consider a simplified version of formulas (23) and (24) under the following assumptions. The energies of the colliding particles are assumed to be so large that the eikonal phases can be neglected. This is true under the condition

$$\bar{V}a/\hbar v \ll 1, \tag{28}$$

where $\bar{V}$ and a are the mean value and the radius of the action of the corresponding potential, and v is the corresponding velocity. Rearrangement reactions were in fact investigated in this high-energy approximation in Ref. 9. Our analysis, however, which is based on the general eikonal formula (3), enables us to show which regions of the action of the pair potentials make the most substantial contribution to any particular mechanism, and consequently to choose the corresponding approximations used in the estimates. In contrast to Ref. 9, we can use in our analysis arbitrary potential functions, including singular potentials. For the latter case we can asume a natural cutoff, which can be realized in a general formula with conservation of the eikonal phases.[10] Bearing in mind this cutoff for the singular potentials, we assume in the general case that the potentials have Fourier transforms.

We consider first the stripping mechanism. In the approximation where all the eikonal phases are equal to zero, we cannot start from the quasiclassical formula (23), and must use a factorized version of the initial formula (3), which is given in Ref. 5 ($\hbar = 1$):

$$f_{mn}(\mathbf{k}_i, \mathbf{k}_f) \approx \frac{\mu_i}{4\pi}\left[\hat{\varphi}_n(\varkappa_2) I_{\mathrm{str}\,1}(\varkappa_1) + \hat{\varphi}_m(\varkappa_1) I_{\mathrm{str}\,2}(\varkappa_2)\right], \tag{29}$$

where $\hat{\varphi}_{n,m}$ are the Fourier transforms of the wave functions of the bound states, while the quantities $I_{c1}(\varkappa_1)$, $I_{c2}(\varkappa_2)$ are defined by the formulas

$$\begin{aligned} I_{\mathrm{str}\,1}(\varkappa_1) &= \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_{13}(\mathbf{p})\hat{\varphi}_m(\varkappa_1-\mathbf{p}) = \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_{13}(\varkappa_1-\mathbf{p})\hat{\varphi}_m(\mathbf{p}), \\ I_{\mathrm{str}\,2}(\varkappa_2) &= \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_2(\mathbf{p})\hat{\varphi}_n(\varkappa_2-\mathbf{p}) = \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_2(\varkappa_2-\mathbf{p})\hat{\varphi}_n(\mathbf{p}); \\ \varkappa_2 &\approx 0, \quad \varkappa_1 \approx \mathbf{k}_i m_1/M_{13}. \end{aligned} \tag{30}$$

For the pickup mechanism we have the corresponding expressions

$$f_{mn}(\mathbf{k}_i, \mathbf{k}_f) \approx \frac{\mu_i}{4\pi}\left[\hat{\varphi}_n(\varkappa_2) I_{\mathrm{pu}\,1}(\varkappa_1) + \hat{\varphi}_m(\varkappa_1) I_{\mathrm{pu}\,2}(\varkappa_2)\right]; \tag{31}$$

$$\begin{aligned} I_{\mathrm{pu}\,1}(\varkappa_1) &= \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_1(\mathbf{p})\hat{\varphi}_m(\varkappa_1-\mathbf{p}) = \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_1(\varkappa_1-\mathbf{p})\hat{\varphi}_m(\mathbf{p}), \\ I_{\mathrm{pu}\,2}(\varkappa_2) &= \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_{23}(\mathbf{p})\hat{\varphi}_n(\varkappa_2-\mathbf{p}) = \int \frac{d\mathbf{p}}{(2\pi)^3} \hat{V}_{23}(\varkappa_2-\mathbf{p})\hat{\varphi}_n(\mathbf{p}); \\ \varkappa_1 &\approx 0, \quad \varkappa_2 \sim \mathbf{k}_i m_3/m_1. \end{aligned} \tag{32}$$

The main contribution to (29) and (30) is made by the terms $\hat{\varphi}_n(\varkappa_2) I_{c1}(\varkappa_1)$ and $\hat{\varphi}_m(\varkappa_1) I_{\Pi 2}(\varkappa_2)$, which contain the Fourier transforms of the potentials V_{13} and V_{23} at short distances. The remaining terms contain Fourier transforms of the potentials V_2 and V_1, respectively, and therefore make a smaller contribution. The angular dependence is determined mainly by the functions $\varphi_n(\varkappa_2)$, $\hat{\varphi}_m(\varkappa_1)$ of the weakly bound states, which have a maximum at zero values of the arguments. The energy dependence of the amplitude is determined mainly by the quantities I_{str} and I_{pu}, and to calculate these quantities we must make additional assumptions concerning the Fourier transforms of the pair potentials at short distances, and on the wave functions.

We use for the wave functions of the strongly bound states the functions of the cut-off harmonic oscillator in the momentum representation

$$\begin{aligned} \varphi_j(\mathbf{p}) &= (16\pi^3\mu\omega)^{1/4} p^{-1} H_j(p/\alpha)\exp(-p^2/2\alpha^2) \\ &\equiv \Phi(p)\exp(-p^2/2\alpha^2), \quad \alpha = (\mu\omega)^{1/2}, \end{aligned} \tag{33}$$

where H_j is the Hermite polynomial of order j, ω is the frequency, and μ is the reduced mass. It is clear that this function is concentrated in the region $p \lesssim p_0 \equiv \alpha$. To estimate the Fourier transforms of the pair potentials we use the asymptotic form frequently employed in the calculations[11]

$$V_{13}(r) \underset{r\to 0}{\approx} A_{13}\exp(-\beta_{13} r), \tag{34}$$

so that

$$\hat{V}_{13}(p) = 8\pi\beta_{13}A_{13}/(p^2+\beta_{13}^2)^2. \tag{35}$$

The corresponding expressions can be used for $\hat{V}_{23}$ in the pickup mechanism. The potential (35) has a smoother behavior than the wave function (33) and can be approximately characterized by an action radius $p_* = \beta_{13}$. At $p_0 \sim p_*$ (light particles) we use the following approximations for $I_{\mathrm{str}1}$ and $I_{\mathrm{pu}2}$:

$$I_{\mathrm{str}\,1} \approx \frac{8\pi\beta_{13}A_{13}\varphi_m(0)}{(\varkappa_1^2+\beta_{13}^2)^2}, \quad I_{\mathrm{pu}\,2} \approx \frac{8\pi\beta_{23}A_{23}\varphi_n(0)}{(\varkappa_2^2+\beta_{23}^2)^2}. \tag{36}$$

Conversely, at $p_0 \gg p_*$ (heavy particles)

$$I_{\mathrm{str}1} \approx A_{13}\hat{\varphi}_m(\varkappa_1), \quad I_{\mathrm{pu}\,2} \approx A_{23}\hat{\varphi}_n(\varkappa_2). \tag{37}$$

When estimating the second and first terms in expressions (29) and (31) respectively, we take into account the fact that $\varphi_{n,m}$ are functions of weakly bound states and their Fourier transforms have sharp maxima near zero. We then have

$$I_{\mathrm{str}\,2} \approx V_2(\varkappa_2)\varphi_n(0), \quad I_{\mathrm{pu}\,1} \approx V_1(\varkappa_1)\varphi_m(0), \tag{38}$$

and it must be remembered that $\hat{V}_{1,2}$ are Fourier transforms of the potentials $V_{1,2}(r)$ at large values of the argument. Choosing as the attraction potentials $V_{1,12}$ the Sutherland potentials, we have (the expression for $\hat{V}_2$ is obtained by making the change of indices $1 \to 2$)

$$\hat{V}_1(\varkappa_1) \approx -4\pi\varepsilon_1\sigma_1[\varkappa_1^2 + (2\sigma_1)^{-2}]^{-1}, \tag{39}$$

where ε_1 is the depth of the potential well and σ_1 is the radius of the hard core. At small values of the arguments we can put approximately

$$\varphi_n(0)\approx{}^4/_3\pi(\mu_{23}\omega_{23})^{3/2}\hat{\varphi}_n(\varkappa_2),\qquad \varphi_m(0)\approx{}^4/_3\pi(\mu_{13}\omega_{13})^{3/2}\hat{\varphi}_m(\varkappa_1) \tag{40}$$

As a result we obtain for the stripping and pickup mechanisms in the case of heavy particles

$$f_{mn}^{\mathrm{str}}=B_s\hat{\varphi}_n(\varkappa_2)\hat{\varphi}_m(\varkappa_1),\quad B_{\mathrm{str}}=\frac{\mu_1}{4\pi}\left[A_{13}-\frac{4\pi}{3}(\mu_{13}\omega_{13})^{3/2}V_2(\varkappa_2)\right], \tag{41}$$

$$f_{mn}^{\mathrm{pu}}=B_s\hat{\varphi}_n(\varkappa_2)\hat{\varphi}_m(\varkappa_1),\quad B_{\mathrm{pu}}=\frac{\mu_1}{4\pi}\left[A_{23}-\frac{4\pi}{3}(\mu_{23}\omega_{23})^{3/2}V_1(\varkappa_1)\right]. \tag{42}$$

We can write down the following general approximate formula for the description of the small-angle scattering:

$$f_{mn}(\mathbf{k}_i,\ \mathbf{k}_f)=M\hat{\varphi}_m(\varkappa_1)\hat{\varphi}_n(\varkappa_2), \tag{43}$$

where $M(\varkappa_1,\varkappa_2)$ should be taken to mean a certain function that depends little on its arguments, such as

$$M=(B_{\mathrm{str}}\varkappa_1^2+B_{\mathrm{pu}}\varkappa_2^2)/(\varkappa_1^2+\varkappa_2^2), \tag{44}$$

which tends to the corresponding constants B_{str} and B_{pu} for the stripping ($\varkappa_2\sim 0$) and pickup ($\varkappa_1\sim 0$) mechanisms. Thus, from (43) and (24) we can calculate the contributions made to the reaction cross section by scattering through angles close to 0 and π. We represent the small momentum transfers $\varkappa_2$ and $\varkappa_1$ for the stripping and knock-out mechanisms respectively by

$$\varkappa_2=2k_i\sin(\theta/2),\qquad \varkappa_1=2k_i\sin(\theta/2). \tag{45}$$

The angle θ in the first expression is between the vectors $\mathbf{k}_i$ and Δ, and in the second it is formally a small angle charterizing the change of $\varkappa_1$ near the eikonal direction. We use next Eq. (28) and represent the wave functions of the weakly bound states in the following approximate form:

$$\hat{\varphi}_A(\varkappa_i)\approx\hat{\varphi}_A(0)\exp\{-\varkappa_i^2/2\alpha_A^2\}. \tag{46}$$

In (46), $\hat{\varphi}_{n,m}(0)$ are the pre-exponential factors that depend little on the angle, and which we calculate at zero values of the arguments. We retain the principal dependence on the angle in the arguments of the exponentials as $k_i\to\infty$. We then have

$$\sigma_{\mathrm{str}}^*(\theta)=\left(\frac{E-E_*}{E}\right)^{1/2}B_{\mathrm{str}}^2\left|\hat{\varphi}_m^*\left(\frac{m_3}{M_{13}}\mathbf{k}_i\right)\hat{\varphi}_n(0)\right|^2\exp\left(-4\frac{\mathbf{k}_i^2}{\alpha_n^2}\sin^2\frac{\theta}{2}\right), \tag{47}$$

$$\sigma_{\mathrm{pu}}(\theta)=\left(\frac{E-E_*}{E}\right)^{1/2}B_{\mathrm{pu}}^2\left|\hat{\varphi}_n\left(\frac{m_3}{m_1}\mathbf{k}_i\right)\hat{\varphi}_m^*(0)\right|^2\exp\left(-4\frac{\mathbf{k}_i^2}{\alpha_m^2}\sin^2\frac{\theta}{2}\right), \tag{48}$$

where E_* is the resonance defect.

When integrating (47) and (48) we make first the substitution $\sin(\theta/2)\to\theta/2$ and extend formally the integration with respect to θ from 0 to ∞ as $k_i\to\infty$. For the total cross sections we then obtain the following approximate expressions[2]:

$$\sigma_{\mathrm{str,pu}}=\frac{\pi}{8}B_{\mathrm{str,pu}}^2\left(\frac{E-E_*}{E}\right)^{1/2}\frac{\alpha_{n,m}^2}{k_i^2}\left|\left\{\begin{matrix}\hat{\varphi}_m^*(m_3\mathbf{k}_i/M_{13})\hat{\varphi}_n(0)\\ \hat{\varphi}_m^*(0)\hat{\varphi}_n(m_3\mathbf{k}_i/m_1)\end{matrix}\right\}\right|^2. \tag{49}$$

To simplify Eqs. (24) and (27) which pertain to the knock-out mechanism, we rewrite the integral (27) in the momentum representation

$$J=\int\frac{d\mathbf{k}}{(2\pi)^3}\exp(-i\mathbf{k}\mathbf{r}_0)\hat{\varphi}_m\left(\frac{\varkappa_1+\varkappa_2}{2}+\mathbf{k}\right)\hat{\varphi}_n\left(\frac{\varkappa_1+\varkappa_2}{2}-\mathbf{k}\right). \tag{50}$$

The main contribution to this integral is made by the region in the vicinity of the origin $kr_0\lesssim 1$, so that we can use the approximation

$$\hat{\varphi}_{n,m}\left(\frac{\varkappa_1+\varkappa_2}{2}\mp\mathbf{k}\right)\approx\hat{\varphi}_{n,m}\left(\frac{\varkappa_1+\varkappa_2}{2}\right)\exp\left\{\mp\frac{\varkappa_1+\varkappa_2}{2\alpha_{n,m}^2}\mathbf{k}-\frac{\mathbf{k}^2}{2\alpha_{n,m}^2}\right\}, \tag{51}$$

in which we retain in the argument of the exponential the terms linear and quadratic in $\mathbf{k}$, and confine ourselves to the zeroth term of the expansion in $\mathbf{k}$ in the pre-exponential factor, following the conclusions of Ref. 12, in which integrals of the type (50) are calculated. Using then the approximate formula of Ref. 12 and putting $\varkappa_1+\varkappa_2\approx 0$ in the pre-exponential factor of (51), we obtain for J the estimate

$$J\approx\frac{\alpha^3}{(2\pi)^{3/2}}\hat{\varphi}_m(0)\hat{\varphi}_n(0)\exp\left\{-\frac{\alpha^2r_0^2}{2}-\frac{\alpha^2(\varkappa_1+\varkappa_2)^2}{2\alpha_n^2\alpha_m^2}\right\},$$
$$\alpha^2=\alpha_n^2\alpha_m^2(\alpha_n^2+\alpha_m^2)^{-1}. \tag{52}$$

Approximating next r_0 and $\mathcal{F}$ respectively with the aid of the expressions for σ_{12} and $\sigma_{12}^2/4$, where σ_{12} is the radius of the hard core of the potential V_{12} (see Ref. 8), and using also the relations $\varkappa_1+\varkappa_2=\Delta m_3/(m_1+m_3)$, $\Delta=2k_i\sin(\theta/2)$, we obtain for the differential knock-out cross section

$$\sigma_{\mathrm{ko}}(\theta)=\left(\frac{E-E_*}{E}\right)^{1/2}B_{\mathrm{ko}}\exp\left(-\frac{4m_3^2}{M_{13}^2}\frac{k_i^2\alpha^2\sin^2(\theta/2)}{\alpha_n^2\alpha_m^2}\right), \tag{53}$$

where

$$B_{\mathrm{ko}}=\frac{\mu_1^2\sigma_{12}^2}{4m_1^2}\left(\frac{\alpha^2}{2\pi}\right)^3|\hat{\varphi}_n(0)\hat{\varphi}_m(0)|^2\exp(-\alpha^2\sigma_{12}^2). \tag{54}$$

Integrating (53) with respect to θ we obtain in the same approximation as before for the total knock-out cross section

$$\sigma_{\mathrm{ko}}=\frac{\pi}{4}\frac{M_{13}^2}{m_3^2}B_s\frac{\alpha_n^2\alpha_m^2}{\alpha^2k_i^2}\left(\frac{E-E_*}{E}\right)^{1/2}. \tag{55}$$

Recognizing that the quantity $2(2\pi)^{-6}\alpha_n^2\alpha_m^2\alpha^2|\varphi_m(0)\varphi_n(0)|^2$ at $\alpha_n\approx\alpha_m$ is of the order of unity, we get

$$\sigma_{\mathrm{ko}}\approx\frac{1}{2}(2\pi)^3\exp(-\alpha^2\sigma_{12}^2)\frac{\alpha^2}{k_i^2}\sigma_{12}^2\left(\frac{E-E_*}{E}\right)^{1/2}. \tag{56}$$

The total cross section of the reaction (2), with account taken of all three mechanisms, can be calculated from the formula

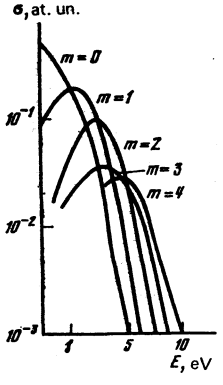

FIG. 1.

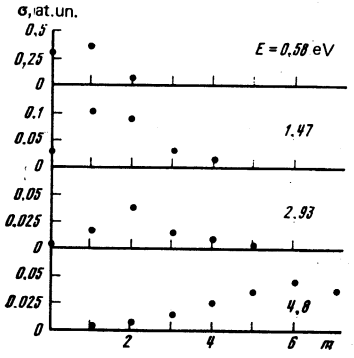

FIG. 2.

$$\sigma_{i\to f}=\sigma_{str}+\sigma_{pu}+\sigma_{ko}. \tag{57}$$

By way of example we consider the process $T+H_2 \to TH+H$, which was investigated in Ref. 13 within the framework of the stripping mechanism on the basis of Faddeev equations. Calculation by formulas (49) and (56) shows that at energies $E \lesssim 10$ eV the contribution of the stripping mechanism predominates, and only the asymptotic form at $E \gtrsim 20$ eV is determined by expression (56). Equation (49) determines the characteristic maximum of the scattering cross section, both with respect to the energy at fixed m, and with respect to m at fixed energy (Figs. 1 and 2). At $E \sim 5$–7 eV, when the conditions for realizing the stripping mechanism are satisfied to the highest degree, Eq. (49) yields results that coincide essentially with those of Ref. 13. Since Eqs. (49) and (56) have all the qualitative distinguishing features that manifest themselves in the more exact calculations, they can be used to estimate the cross sections.

§ 4. ESTIMATES OF THE RATE CONSTANTS OF CHEMICAL REACTIONS AT HIGH ENERGIES

The rate constant of a chemical reaction (per colliding pair) will be calculated from the formula

$$K_{i\to f}=2^{3/2}\pi^{-1/2}\mu^{-1/2}(kT)^{-3/2}\int_{\delta(E_*)}^{\infty} dE\,E e^{-E/kT}\sigma_{i\to f}(E), \tag{58}$$

where $\mu=\mu_1$, $E=\mu k_i^2/2m_1^2$ is the energy of the colliding particles in the c.m.s., $\delta(E_*)=E_*$ at $E_*>0$ and $\delta(E_*)=0$ at $E_*<0$. We confine ourselves to allowance for the contribution of only the stripping mechanism, which is predominant in a wide energy interval, since it is connected with a large region of impact parameters in peripheral collisions. The contributions of the remaining mechanisms are just as easy to estimate. We start from the first equation of (49) for the reaction cross section. Substitution of this equation in (58) with allowance for the representation (33) of the wave function $\hat{\varphi}_m$ yields ($E_*>0$)

$$K_{i\to f}=\frac{\pi^{3/2}}{2}B_{str}^2\alpha_n^2(2\mu kT)^{-3/2}\frac{\mu^2}{m_1^2}\int_{E_*}^{\infty}\left(\frac{E-E_*}{E}\right)^{1/2}$$
$$\times\exp\left(-\frac{q_{str}(T)E}{kT}\right)|\hat{\varphi}_m(\rho_{str}E)\hat{\varphi}_n(0)|^2\,dE,$$
$$q_{str}(T)=1+\frac{\rho_{str}^2kT}{2\alpha_m^2},\quad \rho_{str}=\frac{m_3}{M_{13}}\left(\frac{2m_1^2}{\mu}\right)^{1/2}. \tag{59}$$

As seen from (59), at the lower limit the important role is played by the function $(E-E_*)^{1/2}$, and at the upper limit by the exponential. Therefore we use an approximation in which we take outside the integral sign the remaining smoother functions, which we calculate at $E=E_*$. Then, introducing the new variables $E/kT=\Theta+\Theta_*$, $E_*/kT=\Theta_*$, we have

$$K_{i\to f}=C\mathcal{F}(E_*)\exp(-\Theta_*)\int_0^{\infty}\Theta^{1/2}\exp(-q_{str}\Theta)d\Theta=C\mathcal{F}(E_*)q_{str}^{-3/2}\exp(-\Theta_*),$$
$$C=\pi^{3/2}2^{-1/2}\mu^{-3/2}\left(\frac{\mu}{m_1}\right)^2B_{str}^2\alpha_n^2,\quad \mathcal{F}(E_*)=E_*^{-1/2}|\hat{\varphi}_m(\rho_{str}E_*)\hat{\varphi}_n(0)|^2. \tag{60}$$

In particular, at small kT we obtain the usual Arrhenius law.[11] It should be noted, however, that in the calculation of the macroscopic rate constant, i.e., when averaging over the levels, the Arrhenius law is not obtained in any approximation, owing to the strong dependence of $\mathcal{F}$ on E_*. Equation (60) can be used to obtain data on the scattering cross sections from the experimental data. For example, for the reaction $O+N_2 \to NO+N$ ($D_{N_2}=225$ cal/mole, $D_{NO}=150$ cal/mole) we obtain, for the transition to the ground state $\Theta_*=37\,500/T$, K, $E_*=0.12$ a.u. If we use for the maximum cross section the value 6×10^{-16} cm^{-2} obtained for the $O+N_2$ system by substituting $E=E_*$ in (49), we get in the limit of small kT the estimate

$$K\approx 6.89\cdot10^{13}\exp\left\{-\frac{37\,500}{T\text{K}}\right\}\frac{\text{cm}^3}{\text{mole}\cdot\text{sec}},$$

which differs from the experimental results[14] only by the factor (6.89 → 6.5).

Thus, the proposed theory, obtained by a rather rigorous method in the eikonal approximation, makes it possible to investigate the angular distribution of the products of chemical reactions as functions of the parameters of the potentials and of the wave functions on the basis of explicit analytic formulas of the type (23), (24), (47), and (48). It permits simultaneously to obtain relatively simply theoretical estimates of the rates of chemical reactions at high temperatures, including summation over the vibrational levels of the molecules in the initial and final states. A comparison of the theory with direct experiment on the angular distribution, and also with experimental data for the rate constants of reactions, can yield sufficiently reliable theoretical estimates of the effectiveness of a chemical reaction at high temperatures.

[1)]The work was performed as part of an agreement of creative collaboration of the Leningrad and Stockholm Universities.
[2)]The factor $\hat{\varphi}_n(0)$ is not a well defined quantity for an arbitrary potential model; to avoid misunderstandings, we can assume $\hat{\varphi}_n(0)\equiv\hat{\varphi}_n(\alpha_n)$.

[1]E. E. Nikitin, Teoriya élementarnykh atomno-molekulyarnykh reaktsiĭ (Theory of Elementary Atom-Molecule Reactions), Khimiya, M., 1970.
[2]G. K. Ivanov and Yu. S. Sayasov, Zh. Eksp. Teor. Khim. 3, 172 (1967).
[3]A. V. Bogdanov and G. V. Dubrovskiĭ, Teor. Mat. Fiz. 13, 88 (1972).
[4]G. V. Dubrovskii and A. V. Bogdanov, Zh. Eksp. Teor. Fiz. 64, 1581 (1973) [Sov. Phys. JETP 37, 801 (1973)].

[5]G. V. Dubrovskiy, A. V. Bogdanov, and I. Fischer-Hjalmars, Chem Phys. 7, 405 (1975).
[6]M. V. Fedoryuk, Metod perevala (The Saddle-Point Method), Nauka, 1977.
[7]A. V. Bogdanov and G. V. Dubrovskii, Vestn. Leningr. Univ. Ser. Mater.-Mekh. 19, 69 (1978).
[8]A. V. Bogdanov, Vest. Leningr. Univ. Ser. Mater.-Mekh. 1, 96 (1978).
[9]A. T. Brodskiĭ and V. S. Potapov, Yad. Fiz. 12, 1163 (1970) [Sov. J. Nucl. Phys. 12, 639 (1971)].
[10]I. I. Kholyavin, Vestn. Leningr. Univ. Ser. Mater.-Mekh. 13, 44 (1975).
[11]J. F. Clarke and M. McChesney, Dynamics or Real Gases, Butterworth, 1964.
[12]L. Sirovich, J. Math. Phys. 11, 1365 (1970).
[13]D. A. Micha and P. McGuire, Chem. Phys. Lett. 17, 207, 1.
[14]E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaksatsionnye protsessy v ydarnykh volnakh (Relaxation Processes in Shock Waves), Nauka, 1965.

Translated by J. G. Adashko

Method of pseudo-coherent states in nonlinear quantum systems

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(Submitted 15 March 1979)
Zh. Eksp. Teor. Fiz. 77, 884–898 (September 1979)

A new method is proposed for the study of the behavior of wave packets in various quantum systems, including anharmonic ones. It is shown how to approximate such a packet optimally with the aid of a Gaussian. A closed system of ordinary differential equations is obtained for the position and width of this packet. The proposed method is applicable during the time in which the difference between the true solution and the approximating Gaussian solution is small. Wave packets in both one-dimensional and multidimensional systems are considered. It is shown, with a quantum nonlinear string as an example, how to effect the transition from the multidimensional problem to the field problem. The obtained system of ordinary differential equations can be used to set up a numerical experiment on the excitation of molecules. It is shown how to vary the frequency of the field with time at a given anharmonicity, so as to ensure an effective rapid excitation of an oscillator.

PACS numbers: 03.65.Db

INTRODUCTION

Much attention is being paid recently to the buildup of oscillations in molecules. This question is important for the understanding of the phenomenon of collisionless collective dissociation, of the excitation of molecules by intense light,[1-5] of the excitation of oscillations of the field of surface forces,[6] etc. The behavior of such nonlinear systems in monochromatic fields was considered in a large number of papers (see, e.g., Refs. 7–9).[1)] In Refs. 8 and 9, computer calculations were used to consider both classical and quantum problems dealing with the behavior of a particle in a one-dimensional potential well of non-harmonic type under the influence of an external exciting force. In many of the cases considered in Ref. 8, a curious regularity was observed: despite the relatively strong anharmonicity, the solution in the quantum case was a more or less localized wave packet moving along a trajectory close to classical, but in contrast to the well known coherent state in the harmonic oscillator,[10] the shape of the packet varied with time (the packet pulsated). A situation is possible (and is certainly realized at least during the initial stages of the the excitation), wherein the shape of such localized formations does not deviate noticably from Gaussian. We shall call such wave packets pseudo-coherent states.

In view of the large complexity of the calculation, it is impossible to use directly the method of Refs. 8 and 9 for a numerical experiment on molecules. We propose in this article a method that makes it possible to calculate, in the presence of pseudo-coherent states,[2)] the position and width of a wave packet at each instant of time in both the one-dimensional and miltidimensional cases. Since the method reduces to a solution of a system of ordinary differential equations, it can be used in principle to set up numerical experiments also for multidimensional systems that describe molecules.

When working with pseudo-coherent states we can make use of the following device: we introduce an auxilliary potential $U_1(x,t)$ which, on the one hand, approximates at each instant of time in "optimal" fashion the true potential $U(x,t)$ at the location of the packet [$U_1(x,t)$ can differ quite strongly from $U(x,t)$ in places where there is no packet], and on the other hand greatly simplifies the procedure of solving the Schrödinger equation. We can choose $U_1(x,t)$ to be a potential in the form $\alpha(t)+\beta(t)x+\gamma(t)x^2$.[11] Then, if at the initial instant the packet had a Gaussian form, the solution of the

 0038-5646/79/090446-08$02.40