[1] The requirement that the wave function should satisfy the Dirac equation follows from its construction. By definition the wave function is obtained by multiplying the amplitudes for the formation of the bound states, $A_r^{\pm}$, for given polarization r, and sign of the energy ($\pm$) with the standard spinors $u_r(P)$ and $v_r(P)$: $\psi = \sum_r A_r^+ \mu_r + A_r^- v_r$.

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Theory of vibration–rotation excitation of diatomic molecules in a generalized eikonal method

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A quasiclassical theory of vibration–rotation excitation of molecules is proposed on the basis of a general expression obtained earlier for the scattering amplitude in angle–action variables. For eikonal trajectories, it reduces to a generalized Glauber formula, taking into account internal motion of the target. If the Morse rotating oscillator model is used, the calculation of the differential cross sections reduces to quadratures. Various simplified expressions are derived for the cross sections, including, in particular, a Bessel approximation. This approximation is used to calculate the cross sections of vibrational transitions in the Li^+–H_2 system and of rotational transitions in H_2–H_2 collisions; these cross sections are compared with the experimental values and calculations by the strong coupling method. The comparison indicates a good accuracy of the simplified analytic expressions. The proposed theory may be particularly effective for treating collisions with multiatomic molecules and also with the surface of a solid.

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The development of the theory of vibration–rotation excitation of molecules in collisions with various targets (electron, atom, molecule, solid) is of great interest in connection with investigations with lasers,[1] the study of rotational relaxation in freely expanding jets,[2,3] experiments on molecular beams,[4] the solution of problems concerning the structure of shock waves,[5] etc. This explains the recent publication of many studies on this question.

The main difficulties in calculations of the cross sections of vibration–rotation transitions are due to the multidimensional nature of the problems, and also the circumstance that under the most typical conditions one does not have fulfillment of the conditions of applicability of perturbation theory, $\varepsilon_0 \equiv a_0 \tau_c / \hbar \ll 1$, $\tau_c / \hbar \approx (\Delta E)^{-1}$, or the Massey adiabatic criterion $\eta_0 \equiv \bar{\nu} \tau_c \gg 1$. On the other hand, the condition of the quasiclassical approximation for the relative ($\alpha_0 \equiv KR_0 \gg 1$) and internal motion of the molecules is frequently satisfied. Here, we have denoted by a_0 the mean value of the potential, by R_0 the interaction range of the molecules, by $\bar{\nu}$ the characteristic frequency of the internal motion, by τ_c the collision time, and by ΔE the mean defect of the

resonance. Therefore, to go beyond perturbation theory in the solution of this problem, a number of authors have recently made very laborious numerical calculations based on the approximation of strong channel coupling[6] and the classical trajectory method.[7] The difficulties of carrying out and using such calculations for a large number of pairs in kinetic problems prompted an information-theory approach[8] aimed at establishing simple approximate expressions (containing free parameters) for the cross sections and transport coefficients.

Among the analytic approaches, the most popular has been the exponential approximation for the S matrix in its various forms,[9-13] the basis being provided by the Magnus approximation for the nonstationary propagator. It should however be noted that a rigorous expression for the scattering amplitude in terms of such a propagator has not hitherto been given. Therefore, the heuristic method of introducing the exponential approximation in multidimensional problems leads to fundamental difficulties associated with the use of approximate classical trajectories, the fulfillment of the optical theorem and the symmetry property of the ampli-

tude with respect to the initial and final states, and the treatment of zero-angle scattering and other classically forbidden transitions.

In the present paper, we propose a systematic and rigorous theory of vibration–rotation excitation of diatomic molecules. It is based on the Morse rotating oscillator model[14] and an exact representation for the T operator in angle–action variables obtained recently.[15] The proposed theory simplifies Glauber theory[16] in the sense that it uses a description of the internal motion of the molecules by means of angle–action variables, but at the same time generalizes Glauber theory to the case of lower energies of the relative motion and large scattering angles. On the other hand, it gives the most rigorous quasiclassical representation of the scattering amplitude in terms of a propagator of exponential form on approximate classical trajectories. These modifications in Glauber theory are particularly helpful for problems of gas dynamics and physical kinetics. The proposed theory can be used for problems involving more complicated objects (multiatomic molecules, crystal surfaces,[17] clusters, nonspherical nuclei, etc.). For the simplest form of trajectory (eikonal approximation), the problem is reduced to quadratures containing only the interaction potential, which is very important for studying the influence of different regions of the potential surface on the probability of inelastic transitions.

We obtain and discuss various approximate analytic expressions for the cross sections. We make calculations of the differential cross sections of vibrational ($Li^+ - H_2$) and rotational ($H_2 - H_2$) excitation, and compare these with experimental results and calculations by the strong coupling method. Comparison indicates good accuracy of the simplified variants of the theory in calculations of the cross sections of RT and VT transitions.

1. GENERAL THEORY

To be specific, we shall consider the process of vibration–rotation excitation of diatomic molecules:

$$AB(n_{1i}j_{1i}m_{1i}) + CD(n_{2i}j_{2i}m_{2i}) \rightarrow AB(n_{1f}j_{1f}m_{1f}) + CD(n_{2f}j_{2f}m_{2f}), \quad (1)$$

$$\mathbf{n}_i = (\mathbf{n}_{1i}, \mathbf{n}_{2i}), \quad \mathbf{n}_f = (\mathbf{n}_{1f}, \mathbf{n}_{2f}), \quad \mathbf{n}_s = (n_s j_s m_s), \quad s = 1, 2,$$

where (njm) are the vibrational, rotational, and magnetic quantum numbers. We assume that the classical internal motion of each molecule can be described in terms of angle–action variables φ_s-$\mathbf{I}_s$ ($s = 1, 2$), the vector $\mathbf{I}_s$ of the action variables being related to the vector $\mathbf{n}_s$ of the quantum numbers by the Bohr–Sommerfeld quantization condition (β_s is a constant vector which depends on the nature of the motion)

$$\mathbf{I}_s = \hbar(\mathbf{n}_s + \beta_s). \quad (2)$$

The classical Hamilton function has the form

$$H = \frac{1}{2\mu}\left(P_R^2 + \frac{L^2}{R^2}\right) + \mathcal{H}_1(\mathbf{I}_1) + \mathcal{H}_2(\mathbf{I}_2) + V(\mathbf{R}, \varphi_1, \mathbf{I}_1; \varphi_2, \mathbf{I}_2), \quad (3)$$

$$\boldsymbol{\varphi} = (\varphi_1, \varphi_2), \quad \mathbf{I} = (\mathbf{I}_1, \mathbf{I}_2), \quad \mathcal{H}(\mathbf{I}) = \mathcal{H}_1(\mathbf{I}_1) + \mathcal{H}_2(\mathbf{I}_2),$$

where $\mathbf{R}$, $\mathbf{P}$, and $\mathbf{L}$ are the coordinates, momenta, and angular momenta of the relative motion of the molecules, μ is their reduced mass, and V is the interac-
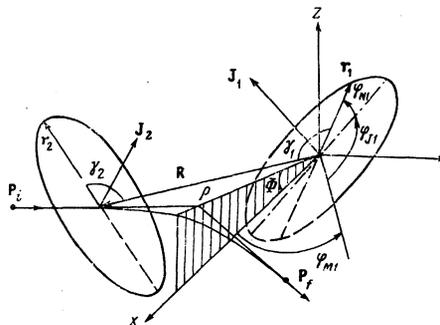
FIG. 1. Collision of two vibrating rotators: φ_{N1}, φ_{J1}, and φ_{M1} are the angular variables of the target in the fixed coordinate system XYZ, ρ is the point of closest approach of the molecules, which lies in the XZ plane, Φ is the azimuthal angle, and γ_1 and γ_2 are the angles between the radius vector $\mathbf{R}$ and the axes of the molecules.

tion potential, which we shall assume consists of an isotropic and an anisotropic part (see Fig. 1)

$$V = V_0(R)[1 + W_1(R; r_1\gamma_1; r_2\gamma_2)], \quad V_1 = V_0 W_1, \quad (4)$$

where γ_s is the angle between $\mathbf{r}_s$ and $\mathbf{R}$.

The equations of the classical trajectory connecting the asymptotic states $\mathbf{n}_i \cdot \mathbf{P}_i$ and $\mathbf{n}_f \cdot \mathbf{P}_f$ must be found from the canonical Hamilton equations with corresponding boundary conditions.[1)] These equations can be conveniently expressed in dimensionless form by introducing the "slow" time $\tau = t/t_0$ ($t_0 = \tau_c$ and $\bar{v}^{-1}$, respectively, for fast and slow collisions):

$$\dot{\boldsymbol{\varphi}}(\tau) = \eta \cdot \mathbf{v}^*(\tau) + \varepsilon_0 \frac{\partial V^*}{\partial \mathbf{n}}, \quad \dot{\mathbf{R}}^*(\tau) = \mathbf{v}^*(\tau),$$

$$\dot{\mathbf{n}}(\tau) = -\varepsilon_0 \frac{\partial V^*}{\partial \boldsymbol{\varphi}}, \quad \dot{\mathbf{P}}^*(\tau) = -\frac{\varepsilon_0}{\alpha_0}\frac{\partial V^*}{\partial \mathbf{R}^*}, \quad (5)$$

$$\mathbf{v}^*(\tau) = \frac{\mathbf{v}(\tau)}{\bar{v}}, \quad \mathbf{v}(\tau) = \frac{\partial \mathcal{H}}{\partial \mathbf{I}}, \quad \mathbf{v}^* = \frac{\mathbf{v}}{\bar{v}}, \quad \mathbf{R}^* = \frac{\mathbf{R}}{R_0}, \quad \eta_* = \nabla t_0, \quad (6)$$

$$\mathbf{P}(-\infty) = \mathbf{P}_i, \quad \mathbf{n}(-\infty) = \mathbf{n}_i, \quad \mathbf{P}(+\infty) = \mathbf{P}_f, \quad \mathbf{n}(+\infty) = \mathbf{n}_f.$$

As can be seen from Eqs. (5), the classical theory contains all three of the previously introduced parameters for fast collisions ($\eta_* = \eta_0 \ll 1$) and only the two small parameters ε and α for slow collisions ($\eta_* \approx 1$). As is pointed out in Ref. 18, the system (5) can be solved for fast collisions by canonical perturbation theory, and for slow collisions by the method of asymptotic averaging with respect to the "fast" variable. Then in the first approximation the theory contains the potential V itself in the case of fast collisions and its periodic part $\tilde{V} = V - \bar{V}$ ($\bar{V}$ is the averaged value of the potential) in the case of slow collisions. It is because of this that one can ensure that the momentum of the perturbation is small for slow collisions.

It is quite clear that on the approximate trajectories one cannot satisfy the boundary conditions (6), and it is therefore important to obtain a representation for the T operator in terms of the solutions of the problem (5)–(6) in which the required increments $\boldsymbol{\Delta} \equiv \mathbf{P}_i - \mathbf{P}_f$ and $\hbar\boldsymbol{\varkappa} = \mathbf{I}_i - \mathbf{I}_f = \Delta\mathbf{I}$ of the quantum numbers are separated from the very beginning and a possibility exists for using approximate trajectories in the calculation of the corresponding quantum transition. Such a representation, obtained in Ref. 15, has the form

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$$\langle P_f n_f | T | P_i n_i \rangle = i \int dR_0 \, d\varphi_0 (P_0/\mu + \nu_0) \delta(\xi_0 q) |\partial(P_0 I_0)/\partial(P_i I_i)|^{1/2}$$

$$\times |\partial(P_0 I_0)/\partial(P_i I_i)|^{1/2} \exp\left[\frac{i}{\hbar}(\Delta R_0 + \Delta I \varphi_0 - \Delta S(R_0, \varphi_0))\right], \qquad (7)$$

$$\xi_0 = (R_0 \varphi_0), \quad q = (\hat{P}_0 I_0), \quad \hat{P}_0 = P_0/P_0, \quad \hat{I}_0 = I_0/I_0, \quad \nu_0 = \nu(I_0),$$

$$\Delta S(R_0, \varphi_0) = \int_{-\infty}^{+\infty} R \, dP(t) + \int_{-\infty}^{+\infty} \varphi \, dI(t) + \int_{-\infty}^{+\infty} V[R_0 + v(t)t, \varphi_0 + \nu(t)t, I(t)] \, dt. \qquad (8)$$

The physical meaning of the expressions (7) and (8) is very simple. Because of the presence of the δ function, the integration in (7) is over the hypersurface $R_0 \cdot \varphi_0$ orthogonal to the trajectories $\xi_0 \perp q$, which we shall call the dynamical plane of the impact parameters. In (7)–(8), ΔS is the increment of the classical action in the "interaction representation",[15] the pre-exponential factors are the Van Vleck determinants for the ingoing and outgoing branches of the trajectory, and P_0 and ν_0 are the values of the relative momentum and modulus of the frequency vector ν on the dynamical plane of the impact parameters. The values of $v(t)$ and $\nu(t)$ are to be taken from the exact solutions of Eqs. (5).

The expression (7) has the following important advantages compared with Miller's S-matrix theory[19]: It introduces the dynamical plane of impact parameters, and it makes it possible to use approximate trajectories, study small-angle scattering, and investigate classically forbidden transitions $P_i n_i \rightarrow P_f n_f$. The problem with classically forbidden transitions reduces to the finding of the complex saddle points of $R_0 \cdot \varphi_0$, at which one joins the two branches of the trajectories on the dynamical plane of the impact parameters for the transitions $P_i n_i \rightarrow P_f n_f$, and to the calculation of their contributions in the framework of the multidimensional method of stationary phase.

In what follows, we shall restrict ourselves to the first order of classical perturbation theory, in the framework of which the ingoing and outgoing branches of a trajectory are characterized by constant values of v, ν, and I, i.e.,

$$v(t), v(t), I(t) = \begin{cases} v_i, \nu_i, I_i, & t < 0 \\ v_f, \nu_f, I_f, & t > 0 \end{cases} \qquad (9)$$

As the dynamical plane of the impact parameters, it is convenient to choose the plane perpendicular to the bisector of the angle between the vectors P_i and P_f. The expression (7) can then be reduced to a Glauber form for the scattering amplitude:

$$f_{n_i n_f}(P_i \rightarrow P_f) = -\frac{iK}{2\pi} \int d\rho \exp(i\Delta\rho) \Gamma_{n_i n_f}(\rho), \quad K = \frac{P_i}{\hbar}, \qquad (10)$$

$$\Gamma_{n_i n_f}(\rho) = \int_0^{[2\pi]} \frac{d\varphi_0}{(2\pi)^q} \exp(i\varkappa\varphi_0) \{\exp[i\Delta S(\rho, \varphi_0)] - \delta_{n_i n_f}\}, \qquad (11)$$

$$\Delta S(\rho, \varphi_0) = -\int_{-\infty}^{+\infty} dt \, V[\rho + v(t)t; \varphi_0 + \nu(t)t; I(t)], \qquad (12)$$

$$R_0 = (\rho, 0), \quad \rho = (\rho, \Phi).$$

In Eqs. (10)–(12), $\Gamma_{n_i n_f}$ is the "inelastic scattering profile", q is the number of dimensions of the space of the angular variables φ_0, and $V_* = V$ and $\tilde{V}$ for fast and slow collisions.

Note that the expressions (7) and (10) (representations of Glauber type) are an alternative to the quasiclassical

representations for the T operator of Schiff type.[18,20]

Under quasiclassical conditions, the main contribution to the increment ΔS of the action is made by the neighborhood of the turning point $t = 0$, where one can use the following approximation for the trajectory of the relative motion (see Fig. 1), this being assumed to lie in the xy plane and described by the isotropic potential V_0 in (4):

$$R = (X, Y, Z), \quad X(t) = \rho \cos \Phi + v_x(t)t + w_x t^2/2, \quad Y(t) = v_y t; \qquad (13)$$
$$Z(t) = \rho \sin \Phi, \quad w_x = -V_0'(\rho)/\mu, \quad v_x(0) = 0.$$

In the eikonal approximation, $w_x = 0$, $v_x = v_{i,f} \sin \theta/2$, $v_y = v_{i,f} \cos \theta/2$. As $v(t)$, $\nu(t)$, and $I(t)$ in the eikonal formulas it is convenient to use the symmetrized expressions

$$v_* = (v_i + v_f)/2, \quad v_* = (\nu_i + \nu_f)/2, \quad I_* = (I_i + I_f)/2$$

or

$$v_* = (v_i v_f)^{1/2}, \quad v_* = (\nu_i \nu_f)^{1/2}, \quad I_* = (I_i I_f)^{1/2}. \qquad (14)$$

Compared with Glauber theory used for problems of this kind,[21,22] the approximate theory based on Eqs. (10)–(12) takes into account the internal motion of the target $(\nu_* \neq 0)$, makes it possible to consider a wider range of variation of the parameters ε and η, and is simpler when applied to complicated systems. Compared with the parameteric method of Ref. 23, the proposed theory, which generalizes the results of Ref. 24 to the three-dimensional case, gives a more correct description of diffraction scattering effects, which become particularly important in the case of the scattering of molecules on a crystalline surface.[17]

We give some simplified variants of Eq. (10). If in accordance with the splitting of the potential (4) we represent ΔS in the form

$$\Delta S = \Delta S_0(\rho) + \Delta S_i(\rho; \varphi_0, I), \quad \Gamma_{n_i n_f} = \exp\left(\frac{i}{\hbar} \Delta S_0\right) \Gamma_{in_i n_f}, \qquad (15)$$

then the scattering amplitude can be expressed as

$$f_{n_i n_f}(\theta) = -\frac{iK}{2\pi} \int_0^\infty \rho \, d\rho$$

$$\times \int_0^{2\pi} d\Phi \exp\left[\frac{i}{\hbar}\left(2\rho P \sin\frac{\theta}{2}\cos\Phi + \Delta S_0(\rho)\right)\right] \Gamma_{in_i n_f}(\rho). \qquad (16)$$

If the function $\Gamma_{in_i n_f}$ depends weakly on the angle Φ and the influence of inelastic transitions on the scattering for $\theta \approx 0$ is unimportant, then (16) can be represented as the convolution of the elastic scattering amplitude and the inelastic scattering profile $\Gamma_{in_i n_f}$:

$$f_{n_i n_f}(\theta) = -iK \int_0^\infty \rho \, d\rho J_0\left(2K\rho \sin\frac{\theta}{2}\right) \Gamma_0(\rho) \Gamma_{in_i n_f}(\rho), \qquad (17)$$
$$\Gamma_0(\rho) = \exp(i\Delta S_0) - 1,$$

where $J_0(x)$ is a Bessel function of zeroth order.

If the integral (16) is calculated by the method of stationary phase and it is assumed that the stationarity point $\rho_0[\rho_0(\theta), \Phi = 0]$ is determined by the argument of the elastic exponential, then we obtain the approximate representation

$$f_{n_i n_f}(\theta) = f_e(\theta) \Gamma_{in_i n_f}[\rho_0(\theta), \Phi = 0], \qquad (18)$$

where $f_e(\theta)$ is the classical elastic scattering amplitude.

Since the eikonal formulas for sufficiently high energies satisfy the optical theorem to good accuracy,[25] we can calculate the total cross sections for scattering of molecules in the state n_i in accordance with the formula

$$\sigma_{n_i} = \frac{4\pi}{K} f_{n_i n_i}(0) = 4 \int d\rho \int_0^{[2\pi]} \frac{d\varphi_0}{(2\pi)^q} \sin^2 \frac{\Delta S(\rho, \varphi_0)}{2}. \qquad (19)$$

Note also that under the condition $2K \gg 1$ we can use the orthogonality of the Bessel functions[25] and, integrating the square of the modulus of the expression (17) over the solid angle, obtain an expression for the total cross section of an inelastic transition in the form of the formula of the impact-parameter method:

$$\sigma_{n_i n_f} = 2\pi \int_0^\infty \rho \, d\rho |\Gamma_{1 n_i n_f}(\rho)|^2. \qquad (20)$$

2. MODELS OF VIBRATION–ROTATION INTERACTION OF DIATOMIC MOLECULES

For a diatomic molecule, a fairly accurate model is the Morse rotating oscillator model in the angle–action variables $\varphi_N \varphi_J \varphi_M$-$NJM$,[14] for which

$$\mathcal{H} \equiv E(N, J) = -\left[\frac{\alpha N}{(2\mu_0)^{1/2}} - \frac{2D - F_1 J^2}{2(D - F_2 J^2)^{1/2}} \right] + F_0 J^2, \qquad (21)$$

$$N = \frac{1}{2\pi} \oint p_r = \left(n + \frac{1}{2} \right) \hbar,$$

$$J = \left(p_\Theta^2 + \frac{p_x^2}{\sin^2 \Theta} \right)^{1/2} = [j(j+1)]^{1/2} \hbar, \quad M = p_x = m\hbar, \qquad (21a)$$

where p_r, p_Θ, p_x are the momenta of the relative motion of the molecule in a spherical coordinate system; μ_0 is the reduced mass of the molecule; α, D, r_0 are the parameters of the Morse potential; and $F_{0,1,2}$ are quantities that can be expressed in terms of α, D, r_0.

Substituting (21a) in (21), we obtain the levels E_{nj} of the vibration–rotation spectrum, these agreeing well with the results of numerical calculation for not too large n. For small values of $F_1 J^2$ and $F_2 J^2$, we obtain

$$\mathcal{H} = -D\zeta_5^2 + \frac{J^2}{2\mu_0 r_0^2}, \quad \zeta = 1 - \frac{2N}{N_0}, \quad N_0 = \frac{2(2\mu_0 D)^{1/2}}{\alpha}, \qquad (22)$$

i.e., the vibrational spectrum of the Morse oscillator and the rotational spectrum of a rigid rotator.

The unperturbed motion $r(t)$ in the molecule is determined by the relations

$$\begin{pmatrix} x(t) \\ y(t) \\ z(t) \end{pmatrix} = r(t) \begin{pmatrix} -\sin \Psi(t) \sin \varphi_{0M} + \lambda \cos \Psi(t) \cos \varphi_{0M} \\ \sin \Psi(t) \cos \varphi_{0M} + \lambda \cos \Psi(t) \sin \varphi_{0M} \\ (1 - \lambda^2)^{1/2} \cos \Psi(t) \end{pmatrix}, \quad \lambda = \frac{M}{J}; \qquad (23)$$

$$r(t) = r_0 - \alpha^{-1} \ln \xi(t), \quad \xi(t) = (-2a)[b + (b^2 - 4ac)^{1/2} \sin (\varphi_{0N} + \nu_N t)]; \qquad (24)$$

$$\Psi(t) = \nu_J t + J\Lambda[\xi(t)], \quad a = E - F_0 J^2, \quad b = 2D - F_1 J^2, \quad c = -D + F_2 J^2.$$

In Eqs. (23) and (24), we do not write out the explicit form of the functions $\Lambda(\xi)$,[14] $\varphi_0 = (\varphi_{0N}, \varphi_{0J}, \varphi_{0M})$, $\nu = (\nu_N \nu_J; \nu_M = 0)$.

The trajectories of the motion described by Eqs. (23) and (24) also agree well with the results of numerical calculations for not too large n.

As $\alpha \to \infty$ and $\nu_N \to 0$,

$$F_0 \to 1/2\mu_0 r_0^2, \quad F_{1,2} \to 0, \quad \Lambda(\xi) \to 0,$$

and we obtain the trajectories of a rigid rotator. For $J = 0$, we have the equation for the trajectory of a spherical Morse oscillator:

$$r(t) = r_0 + \alpha^{-1} \ln \{\zeta^{-2}[1 + (1 - \zeta^2)^{1/2} \sin (\varphi_{0N} + \nu_N t)]\}. \qquad (25)$$

The further analysis of the problem is determined to a large degree by the models chosen for the isotropic and anisotropic parts of the potential. Whereas there is extensive theoretical and experimental material for an isotropic potential (see, for example, Ref. 26), the choice of the potential determining the inelastic transition presents great difficulties.

The problem is simplified if an inelastic, purely rotational transition is determined by the long-range multipole part of the potential (charge–dipole, charge–quadrupole, dipole–dipole, etc.), which has the form, respectively,

$$V_1 = \frac{Q \, d P_1(\cos \gamma)}{R^2}, \quad V_1 = \frac{Q \Upsilon P_2(\cos \gamma)}{R^3}$$

$$V_1 = \frac{[3 P_1(\cos \gamma_1) P_1(\cos \gamma_2) - P_1(\cos \gamma_0)] d_1 d_2}{R^3} \qquad (26)$$

Here, γ_i and γ_0 are, respectively, the angles between R, d_i, and $d_1 \cdot d_2$; Q, d, and Υ are, respectively, the charge, dipole, and quadrupole moments; $P_s(x)$ are Legendre polynomials.

A more general form of the potential energy surface is frequently expressed in the form[27]

$$V = V_0(R) \sum_j W_j(R) [A_j P_j(\cos \gamma_1) + B_j P_j(\cos \gamma_2)], \qquad (27)$$

where $j = 2K$ $(A_j = B_j)$ and $j = 2K + 1$ $(A_j \neq B_j)$, respectively, for homo- and heteronuclear molecules. It is readily seen that for additive potentials of the form (27) the inelastic scattering profile $\Gamma_{1 n_i n_f}$ factorizes, i.e.,

$$\Gamma_{in} = \Gamma_{1 n_i n_f} = \Gamma_{n_i(1)}^{n_f(1)} \Gamma_{n_i(2)}^{n_f(2)}. \qquad (28)$$

One can also use the additive scheme of two-body potentials,[26] which leads to (27) and additional crossed terms. The additive potentials (27) and the representation (28) are not, in general, suitable for calculating quantum exchange cross sections (VV and RR processes). For such transitions, it is necessary to take into account the crossed terms. In addition, the accuracy of the approximation which uses angle–action variables for quantum exchange processes requires further investigation.

Even greater difficulty is presented by the choice of the potentials V_1, which depend on r_1 and r_2, in the calculation of vibration–rotation transitions (see, for example, Ref. 25). For the simpler problems of vibrational excitation, one frequently uses a "breathing sphere" potential of the form

$$V = V_0(R) + W_1(R) \{A_1 \exp [-\beta_1(r_1 - r_{10})] + B_1 \exp [-\beta_2(r_2 - r_{20})]\}. \qquad (29)$$

To express the potential V in angle–action variables, we use Eqs. (13) and (23), and also the relation

$$\cos \gamma = \mathbf{R}(t) \mathbf{r}(t) / [R(t) r(t)]. \qquad (30)$$

The subsequent and more detailed analysis is made more conveniently for a number of concrete cases.

3. ROTATIONAL AND VIBRATIONAL EXCITATION OF DIATOMIC MOLECULES

1. To describe rotational excitation of diatomic molecules when the vibrational levels are not excited, we proceed from the model of a rigid rotator with interaction potential V_1 of one of the types (26) and (27). For the "rotational excitation profile" of one molecule, we then have the expression

$$\Gamma_{j_i m_i}^{j_f m_f}(\rho, \Phi) = \int_0^{2\pi} \frac{d\varphi_{0M}}{2\pi} \exp(i\varkappa_M \varphi_{0M}) \Gamma_{j_i}^{j_f}(\varphi_{0M}; \theta, \rho, \Phi), \tag{31}$$

$$\Gamma_{j_i}^{j_f} = \int_0^{2\pi} \frac{d\varphi_{0J}}{2\pi} \exp[i\varkappa_J \varphi_{0J} + i\Psi(\varphi_{0J}; \theta, \rho, \Phi)], \quad \varkappa_J = j_i - j_f. \tag{32}$$

The integral (31) describes basically transitions between different values of m; the integral (32), transitions between different values of j. For Ψ, we can obtain the general expression

$$\Psi = C_p \cos(p\varphi_{0J} + \zeta_0), \quad p = 1, 2, \tag{33}$$

where, as is readily seen, C_p and ζ_0 can be expressed in terms of integrals of the form

$$\zeta = \int_{-\infty}^{+\infty} dt \, \frac{W_p[R(t)]}{R^p(t)} \begin{Bmatrix} X^p(t) \\ Y^p(t) \\ Z^p(t) \end{Bmatrix} \lambda(t) \begin{Bmatrix} \sin(pv(t)t) \\ \cos(pv(t)t) \end{Bmatrix}. \tag{34}$$

In (33)–(34), $p = 1, 2$, respectively, for hetero- and homonuclear molecules; $W_p(R)$ is the coefficient of $\cos\gamma$.

Using the well-known integral representation for the Bessel functions,[29]

$$J_\varkappa(z) = \frac{1}{2\pi} \int_{-\tau_* + i\infty}^{-\tau_* + 2\pi + i\infty} \exp\left[iz \cos t + i\varkappa\left(t - \frac{\pi}{2}\right)\right], \tag{35}$$

and also the arbitrariness in the choice of τ_* ($0 \leqslant \tau_* \leqslant \pi$) and the integral nature of $\varkappa$, we readily obtain an explicit expression for $\Gamma_{j_i}^{j_f}$:

$$\Gamma_{j_i}^{j_f} = \exp\left(-\frac{i\varkappa_J \zeta_0}{p} + \frac{i\varkappa_J \pi}{p}\right) J_{\varkappa_J/p}(C_p). \tag{36}$$

The Bessel approximation for the profile (36), which is used in one-dimensional problems,[30-32] gives in conjunction with (16)–(18) the most rigorous expression for the excitation amplitude in the first order of perturbation theory. The Bessel approximation is generalized to the three-dimensional case in Ref. 33, but the not entirely rigorous derivation of the basic expression for the amplitude leads to a different argument of the Bessel function. This difference between the basic expressions for the T operator will also have an influence when the following orders of perturbation theory are taken into account.

We introduce further the simplifying assumption that the main contribution to the cross section is made by planar configurations of the system, when the plane of the rotator lies in the scattering plane [$\lambda(t) \approx 1$]. We shall also assume that the rotation frequency of the rotator is constant and equal to v_*. Under these assumptions, we obtain the approximate equations

$$\cos\gamma \approx \cos\Phi \cos\varphi_J, \quad \varphi_J = v_* t + \varphi_{J0}, \quad R(t) = (\rho^2 + \varepsilon_*^2 t^2)^{\frac{1}{2}}; \tag{37}$$

$$\varepsilon_*^2 = w_* \rho \cos\Phi + v_*^2 \cos^2(\theta/2), \quad w_x = -\partial V_0(\rho)/\partial\rho.$$

The calculations then simplify considerably and lead to the results

$$\Gamma_{j_i m_i}^{j_f m_f} = \delta_{m_i m_f} \exp(iZ_p) J_{\varkappa_J/p}(C_p), \tag{38}$$

$$Z_1 = 0, \quad Z_2 = -\frac{\cos^2\Phi}{2} \int_{-\infty}^{+\infty} W_2[R(t)] \, dt,$$

$$C_p = -\frac{\cos^p\Phi}{p} \int_{-\infty}^{+\infty} W_p[R(t)] \cos(v_* t) \, dt. \tag{39}$$

For the case of a power-law dependence $W_p(R)$, we obtain explicit expressions for Z_2 and C_p:

$$W_p(R) = AR^{-2s} \quad Z_2 = -\frac{\pi(2s-3)!!}{2(2s-2)!!} \cos^2\Phi \, \frac{\rho}{\varepsilon_*} W_2(\rho),$$

$$C_p = -\frac{4\pi}{2^{2s}(s-1)!} \frac{\cos^p\Phi}{p} \frac{\rho}{\varepsilon_*} W_p(\rho) \exp\left(-\frac{pv\rho}{\varepsilon_*}\right)$$

$$\times \sum_{k=0}^{s-1} \frac{(2s-k-2)!}{k!(s-k-1)!} \left(\frac{2pv\rho}{\varepsilon_*}\right)^k; \tag{40}$$

$$W_p(R) = AR^{-2s-1}, \quad Z_2 = -\frac{(2s+1)!!}{2^{s-1}} \cos^2\Phi \, \frac{\rho}{\varepsilon_*} W_2(\rho),$$

$$C_p = -\frac{\pi^{1/2}}{2^{s-1}\Gamma(s+1/2)} \frac{\cos^p\Phi}{p} W_p(\rho) \left(\frac{pv\rho}{\varepsilon_*}\right)^s K_s\left(\frac{pv\rho}{\varepsilon_*}\right), \tag{41}$$

where $K_s(x)$ is a MacDonald function. One can write down more accurate expressions for $\cos\gamma$ and the quantities Z_2 and C_p associated with them by taking into account the variation of R near the turning point, but we shall not dwell on this.

a). For the case of excitation of the rotational levels of a dipole molecule by a charged particle of charge Q we have ($s = 1$)

$$Z_2 = 0, \quad C_1 = -\cos\Phi \frac{\pi Q d}{\varepsilon_* \rho} \exp\left(-\frac{v\rho}{\varepsilon_*}\right), \quad \Gamma_{1j_i j_f} = J_\varkappa(C_1), \quad \varkappa = |j_i - j_f|. \tag{42}$$

Substituting (42) in (16), we find an explicit expression for the scattering amplitude as a double integral with respect to ρ and Φ. In the expression for C_1, we can ignore the dependence on Φ ($\cos\Phi \approx 1$) and then use the expression (17). If we also assume that $\varepsilon_* \approx v_*$, then the total scattering cross section for $2K \gg 1$ can be calculated in accordance with (20).

b). For quadrupole potential ($s = 1$)

$$Z_2 = -\frac{3Q\Upsilon \cos^2\Phi}{4\varepsilon_* \rho^2}, \quad C_2 = -\frac{3v_* Q\Upsilon}{\varepsilon_*^2 \rho} \cos^2\Phi K_1\left(\frac{2v_* \rho}{\varepsilon_*}\right). \tag{43}$$

c). For the additive scheme of the potential (27), the corresponding expressions for $\Gamma_{1j_i j_f}$ with $p = 1, 2$ are obtained by using the expressions (40) and (41).

d). The most complicated expression for the inelastic scattering profile in nonfactorized form is obtained for the dipole–dipole interaction (27) or in the model with crossed terms. In the framework of the simplifications formulated above, we can use the following approximate equations in its calculation:

$$\cos\gamma_1 = \cos\Phi \cos\varphi_{J1}, \quad \cos\gamma_2 = \cos\Phi \cos\varphi_{J2}, \quad \cos\gamma_0 = \cos(\varphi_{J1} - \varphi_{J2}),$$
$$\varphi_{J1} = v_1 t + \varphi_{J10}, \quad \varphi_{J2} = v_2 t + \varphi_{J20}. \tag{44}$$

2. We obtain a simple expression for the "vibrational excitation profile" if we use the breathing sphere potential in the following form in the problem of vibrational excitation of a diatomic molecule by an atom:

$$V(R, r) = V_0(R) + W(R) \exp[\alpha(r - r_0)], \quad W(R) = CR^{-2s}. \tag{45}$$

Using (25), we again obtain an expression for the profile in terms of a Bessel function:

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$$\Gamma_{1n_in_f} = J_\varkappa(C_k), \quad \varkappa = |n_i - n_f|,$$

$$C_k = \frac{4\pi^{1/2}}{\Gamma(s)} \frac{(1-\zeta^2)^{1/2}}{\zeta^2} \frac{W(\rho)}{\nu_*} \left(\frac{\rho\nu_*}{\varepsilon_*}\right)^{s+1/2} K_{s-1/2}\left(\frac{\rho\nu_*}{\varepsilon_*}\right). \quad (46)$$

Note that in the framework of the approximation (38) we obtain essentially the cross section of the transition $0 \to \varkappa = |j_i - j_f|[\sigma_{0,\varkappa}(\theta)]$. In the adiabatic approximation, the cross section of a transition between arbitrary rotational quantum numbers can be calculated in accordance with the formula[34,35]

$$\sigma_{j_i j_f}(\theta) = \frac{K_f}{K_i}(2j_f+1) \sum_{\varkappa'=|j_i-j_f|}^{j_i+j_f} \begin{pmatrix} j_i & \varkappa' & j_f \\ 0 & 0 & 0 \end{pmatrix} \sigma_{0,\varkappa'}(\theta). \quad (47)$$

4. VIBRATIONAL EXCITATION IN THE Li$^+$—H$_2$ SYSTEM

As an example of the use of the simple expressions (18) and (46), we calculated the differential cross section of vibrational excitation in the Li$^+$–H$_2$ system. For the parameters of the potential (45), we chose here the following values obtained by comparing (45) with other analytic representations of the potential energy surface[36]:

$$s=2, \quad C=4.7\cdot10^{-2} \text{ a. u.}, \quad \beta\approx 2d\approx 1 \text{ a. u.},$$
$$D=0.15 \text{ a. u.}, \quad r_e=0.7 \text{ a.u.},$$

The values for the turning point for large scattering angles were calculated in accordance with[37]

$$\rho(\theta) = C^{1/2s}\left[1 + \frac{1}{2s}\ln\left(\frac{1}{2E}(\pi s)^{1/2}\sin^{-1}\frac{\theta}{2}\right)\right]. \quad (48)$$

The results of the calculations together with the results of the experimental measurements are shown in Fig. 2. The experiment led to measurement of the quantity[38]

$$I(\theta) = \frac{d\sigma}{d\Omega}(0\to n) \Big/ \sum_{v=0}^{n} \frac{d\sigma}{d\Omega}(0\to v)$$

for the energy values $E = 3.65$, 5.54, and 8.8 eV in the

FIG. 3. $(d\sigma/d\Omega)_{pp}(00\to 02|\theta)$ for H$_2$—H$_2$ at $E = 0.1$ eV (a) and 0.3 eV (b). The broken curves show the calculation by the strong coupling method,[6] the continuous curves the calculations in accordance with Eqs. (18), (28), and (36).

range of angles from 125 to 167°. The error of the measurements was ±20% and more and increased with increasing energy and decreasing angle. As can be seen in Fig. 2, the agreement between the calculation based on the simple analytic formula and the experiment can be regarded as satisfactory for all the transitions and considered energies.

5. ROTATIONAL EXCITATION IN THE H$_2$—H$_2$ SYSTEM

To illustrate the method, we can also compare a calculation of the differential cross section of rotational excitation in the H$_2$–H$_2$ system on the basis of the simplified expressions (18), (28), and (36) with the results

FIG. 2. $I(\theta) = (d\sigma/d\Omega)(0\to n)\sum_{v=0}^{n}(d\sigma/d\Omega)(0\to v)$ for Li$^+$—H$_2$ at $E = 3.65$ eV (a), 5.54 eV (b), and 8.8 eV (c). The broken lines show the experimental data of Ref. 37, the continuous lines the calculations in accordance with (18) and (46).
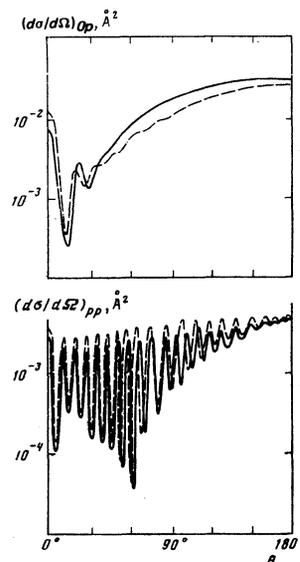
FIG. 4. $(d\sigma/d\Omega)_{0p}(10\to 12|\theta)$ at $E = 0.0929$ eV and $(d\sigma/d\Omega)_{pp}$ $(02\to 24|\theta)$ at $E = 0.55$ eV for H$_2$—H$_2$. The broken curves show the calculation by the strong coupling method,[6] the continuous curves the calculation in accordance with Eqs. (18), (28), and (36).

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of calculation by the strong coupling method[6] (see Figs. 3 and 4). We took the potential model[6]

$$V(R, \gamma_1, \gamma_2)$$
$$= V_0(R)\{1 + B[P_2(\cos \gamma_1) + P_2(\cos \gamma_2)]\},$$
$$V_0(R) = Ae^{-\alpha R}, \quad A = 2.168 \text{ a.u.},$$
$$\alpha = 1.783 \text{ a.u.}, \quad B = 0.14, \tag{49}$$

and considered the differential cross section for collisions of para-para $(d\sigma/d\Omega)_{pp}$, and ortho-para, $(d\sigma/d\Omega)_{op}$, H_2 molecules. In both cases, the scattering amplitude was calculated by symmetrizing the original amplitudes (see Ref. 6)

$$\bar{f}(j_1 j_2 \to j_1' j_2' | \theta) = f(j_1 j_2 \to j_1' j_2' | \theta) + f(j_1 j_2 \to j_2' j_1' | \pi - \theta). \tag{50}$$

The turning points $\rho(\theta)$ were calculated on the basis of the following approximate formulas for the exponential potential:

$$\theta = -\frac{b}{E} A\alpha K_0(\alpha b), \quad \rho(\theta) = \frac{b}{\cos(\theta/2)}, \tag{51}$$

which ensure good accuracy for $\theta \lesssim 30°-40°$.

Finally, the cross sections were calculated in accordance with a formula that takes into account the correction g (see Ref. 6),

$$\frac{d\sigma}{d\Omega}(j_1 j_2 \to j_1' j_2' | \theta) = \frac{K_{j_1 j_2}}{K_{j_1' j_2'}} g(j_1 j_2; j_1' j_2') |\bar{f}(j_1 j_2 \to j_1' j_2' | \theta)|^2;$$
$$K_{j_1 j_2}^2 = \frac{2m}{\hbar}(E - E_{j_1} - E_{j_2}), \quad g(j_1 j_2; j_1' j_2') = \left[\frac{(2j_1'+1)(2j_2'+1)}{(2j_1+1)(2j_2+1)}\right]^{1/2}, \tag{52}$$

this being done for a number of transitions and energies, which are indicated in Figs. 3 and 4.

As can be seen from Figs. 3 and 4, there is good agreement between the proposed simplified theory and the strong coupling method for all the considered cases of inelastic transitions not associated with exchange of quanta, when the potential (49) can be assumed to be a good approximation of the potential surface.

It is interesting to note that the oscillation structure of the cross sections, explained in Ref. 6 by the phase difference between the direct and exchange amplitudes, is described here by the Bessel function, whose argument is equal to the increment of the "inelastic action."

The agreement with the calculation by the strong coupling method is better at small angles and somewhat less good at $\theta \approx \pi/2$, which is due to the approximation (51) and the approximate representation of the trajectories. The agreement obtained for all the considered cases should be regarded as lending support to the Bessel approximation, which gives a fairly accurate description of the probabilities of rotational transitions under conditions when perturbation theory fails.

In this connection, it would be of considerable interest to consider more complicated problems and effects in the framework of the proposed theory, which admits numerous obvious generalizations.

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[1]) These trajectories are real if the transition is classically allowed and complex if it is classically forbidden.

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