Quasiclassical approximation for the inelastic atom-molecule scattering amplitudes

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Exact expressions for the transition probability amplitudes are presented in the form of Feynman path integrals, and their quasiclassical approximations are given. The quasiclassical representations obtained for the transition amplitudes in terms of the quasiclassical action in the action-angle variables are used to study a wide range of multidimensional problems with real interaction potentials (vibrational-rotational transitions in molecules, collisions of particles with a surface, etc.). Perturbation theory techniques for finding the classical action in the cases of fast and slow collisions are developed. As examples of the solution of multidimensional problems with real interaction potentials (vibrational-rotational transitions in molecules, collisions of particles with a surface, etc.). Perturbation theory techniques for finding the classical action in the cases of fast and slow collisions are developed. As examples of the solution of multidimensional problems, analytic expressions are obtained in terms of Bessel functions for the differential cross sections for excitation of hydrogen by a charged particle and of the rotational degrees of freedom of the molecule in the $Li^+ + H_2$ collision, and also for the total cross sections for excitation of the high-lying hydrogen levels in H+H collisions.

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It is convenient to use the multidimensional quasiclassical method in angle-action variables in computations of the vibrational–rotational transitions in molecules, the excitation of hydrogen-like states by charged and neutral particles, the collisions of particles with surfaces, etc. This method has been applied largely in the linear three-body problem (see Miller's review article[1]), where numerical computations of the classical trajectories have been effectively used. Considerably less attention has been given to the question of the computation of the scattering amplitudes in a more realistic three-dimensional collision model. In this case there arise additional complications connected with the derivation of convenient quasiclassical representations for the scattering amplitude, with the approximate computations of the classical action S and the remaining multidimensional integrals, as well as with the analytic continuation of the results obtained in the complex-parameter region in the computation of the classically forbidden transitions.

In the present paper we briefly analyze the various forms of the exact expressions for the transition amplitudes in the form of Feynman path integrals and the quasiclassical representations obtained from these expressions with the aid of the stationary-phase method. Classical perturbation theory techniques are formulated which allow us to find the classical action for fast and slow collisions.

The derivations of the theory, which is suitable for carrying out specific calculations, are illustrated by solving specific physical problems: the computation of the differential cross section for excitation of the hydrogen atom by a fast charged particle, the computation of the total cross section for excitation of the high-lying states in the collision of two hydrogen atoms, and the computation of rotational transitions in diatomic molecules. In the first case, as it turns out, the correction for the internal motion of the target removes the earlier noted divergence of the zero-angle eikonal amplitudes in the case of charged particles.[2] A comparison is carried out with experiment and with the data of other authors. In the second case the found total cross sections can be of interest in connection with the study of the relaxation processes in a hydrogen plasma. The computed cross sections for the rotational transitions in the $Li^+ - H_2$ system are in good agreement with experiment, and demonstrate the accuracy of the method.

1. EXACT EXPRESSIONS FOR THE SCATTERING AMPLITUDE IN THE FORM OF PATH INTEGRALS AND THEIR QUASICLASSICAL APPROXIMATIONS

Let us give some exact expressions for the scattering amplitude in the form of Feynman path integrals on the basis of the results of Ref. 3, where we refer the reader for certain mathematical details of their derivation.

We shall proceed from the well-known continuous representation for the amplitude of the transition $i \to f$ during the finite time interval $t - t'$[4,5]:

$$a_{if}(t', t) = \iint dq\, dq'\, \Psi_f^*(q, t)\, \Psi_i(q', t') \int D\Gamma \exp\left[\frac{i}{\hbar} S(qt, q't')\right],$$

$$S(qt, q't') = \int \tilde{p}(\sigma)\, d\tilde{q}(\sigma) - \int_{t'}^{t} H[\tilde{p}(\sigma), \tilde{q}(\sigma), \sigma]\, d\sigma, \qquad (1)$$

where q' and q denote the sets of initial and final Cartesian coordinates in configuration space, the $\Psi_{i,f}$ are the initial and final wave functions of the unperturbed Hamiltonian, and $\int D\Gamma$ denotes a functional integral in the phase space (q, p), which can be understood, for example, in the sense of a finite-multiple approximation.[4] The representation (1), which is in the form of an integral over paths with given coordinate ends q' and q, is general, and is suitable for both nonstationary and stationary perturbations.

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In the stationary case, to obtain the T matrix, which is connected with the S matrix by the relation

$$S_{if}=\delta(i-f)-2\pi i\delta(E_i-E_f)T_{if},$$
$$S_{if}=\lim_{t'\to-\infty,\ t\to+\infty}a_{if}(t',t), \tag{2}$$

it is necessary to accomplish the passage to the limit $t'\to-\infty$, $t\to+\infty$, and separate out the two δ-functions figuring in (2). The actual accomplishment of this procedure depends on the form of the functions $\Psi_{i,f}$, and has been carried out for the case of elastic scattering in Ref. 6.

In the case of elastic scattering or the problem of excitation involving the use of the angle-action (φ-I) variables, the bound-state wave functions $\Psi_{i,f}$[7] can be written in the form (C is a normalization constant)

$$\Psi_{i,f}(qt)=C\exp\left[\frac{i}{\hbar}p_{i,f}q-\frac{i}{\hbar}E_{i,f}t\right],\quad p_i\equiv p',\quad p_f\equiv p. \tag{3}$$

Further, taking into account the easily verifiable—for example, in the framework of the finite-multiple approximation—relation

$$p'q'-pq+S(qt,q't')=-\int_{p'}^{p}\tilde{q}(\sigma)d\tilde{p}(\sigma)-\int_{t'}^{t}Hd\sigma\equiv-S(pt,p't') \tag{4}$$

and including the integration over the starting and end points q', q in the functional integral (1), we have

$$a_{if}(t',t)=\int D\Gamma\exp\left\{-\frac{i}{\hbar}[S(pt,p't')-E_ft+E_it']\right\}.$$

Here the functional integration is performed over classical trajectories with given initial and final momenta.

Notice that the equality (4) is exact for elastic scattering and formal for the problem of excitation, since we discarded the exponential tails of the bound-state wave functions, did not prove the canonical invariance of the integral (1) with respect to the angle-action variables, etc. The expression (4) is justified in this case by the fact that, first, the quasiclassical approximation (4) coincides with the one that is obtained when we apply the stationary-phase method ($\hbar\to0$) to (1) and then go over to the angle-action variables with the aid of the well-known rules of transformation from one representation to another. Such considerations were essentially used in Miller's papers,[1] where the "classical S matrix" was obtained from (4) by the stationary-phase method. In this case the passage to the $t'\to-\infty$, $t\to+\infty$ limit can be accomplished on even real classical trajectories. Secondly, as has been shown in practical computations, the "subbarrier" asymptotic form of $\Psi_{i,f}$, which is important for the computation of the classically forbidden transitions, can be taken into account by means of an analytic continuation of the final expressions into the complex-parameter regions (see, in this connection, Refs. 8 and 9). The exact continuous T-matrix representation for the inelastic processes in terms of the abbreviated action S_0 was obtained by another method in Refs. 10, 11, and 3, and has the form (for definiteness, we consider the case of excitation)

$$T_{if}=\iint dq\,dq'\,W(q)\Phi_f^*(q)\Phi_i(q')\cdot\int\{D\Gamma\}_{\mathscr{H}=E}\exp\left[\frac{i}{\hbar}S_0(q,q')\right]. \tag{5}$$

Here the $\Phi_{i,f}$ are the wave functions of the initial and final states, S_0 is the abbreviated action, and $\int\{D\Gamma\}_{\mathscr{H}=E}$ denotes the functional integral over trajectories lying "on the average" on the energy surface $\mathscr{H}=E$. In the $\hbar\to0$ limit $\mathscr{H}$ coincides with the Hamiltonian function H.

Let us now proceed to the quasiclassical expressions for the transition amplitude $a_{if}(t',t)$ and T_{if} for $\hbar\to0$ on the basis of the expressions (1) and (5), respectively, and in the approximation (3) for the bound-state wave functions (in the angle-action variables). Let us separate out from the functional integral (1) or (4) one integration over an intermediate point q^* and apply to the remaining functional integrals the stationary-phase method in the vicinity of a nondegenerate classical trajectory (for details of such computations, see Ref. 3). As a result, we obtain, as is easy to verify (B is a normalization constant that depends on the dimensionality of the space)

$$a_{if}(t',t)\approx B\int dq^*\left|\frac{\partial q}{\partial q^*}\right|^{1/2}\left|\frac{\partial p_-^*}{\partial p'}\right|^{1/2}$$
$$\times\exp\left[\frac{i}{\hbar}(\Delta q^*-\Delta Et+\Delta S_-+\Delta S_+)\right], \tag{6}$$
$$\Delta E=E_i-E_f,\qquad\Delta=p'-p;$$

$$\Delta S_-=\int_{q'}^{q^*}(\tilde{p}-p')d\tilde{q}-\int_{t'}^{t}[H(\sigma)-E_i]d\sigma,$$
$$\Delta S_+=\int_{q^*}^{q}(\tilde{p}-p)d\tilde{q}-\int_{t^*}^{t}[H(\sigma)-E_f]d\sigma, \tag{7}$$

In these formulas $|\partial q/\partial q^*|$ and $|\partial p_-^*/\partial p'|$ are the corresponding transformation Jacobians, which can be expressed in terms of the derivatives of $\Delta S_\pm$ with respect to the initial and final coordinates, the $\Delta S_\pm$ are the increments in the classical action over the ingoing and outgoing branches of the trajectories, and Δ and ΔE are the given increments in the momenta and the energy. The expression (6) is similar to Marcus's formula,[7] but has been derived more rigorously from a continuous integral and is applicable to the case of nonstationary perturbations. Because the momenta p_-^* and p_+^* are different, the two branches of the path are not assumed to be joined. For $q^*=q$ or $q^*=q'$, we obtain a representation of the "final" or "initial" coordinate point and, upon the computation of the integral over q^* by the stationary-phase method ($q^*=q$), the classical Miller S matrix[1] ($t\to-\infty$, $t\to+\infty$) provided the stationary-phase point q_c^* is real (i.e., the transition is classically allowed). When account is taken of the complex stationary-phase points, we obtain, in principle, classically forbidden transitions. The expression (6) can also be used to derive different isometric representations.

In deriving a similar representation for the scattering amplitude (T matrix), we shall proceed from the expression (5) in the angle-action (φ-I[12]) variables. In contrast to the earlier considered case, the end point q is now separated out by the presence of the potential $W(q)$, and the initial and final configurations are characterized by different potentials, $W_{n,m}=W(\mathrm{I}_{n,m},\ \varphi,\ \mathrm{R})$, since the action variable I assumes different values $I_{n,m}$ in the entrance and exit channels (in analogy to the rearrangement reaction in the eikonal approximation[13-15]). Separating out an intermediate coordinate point ($\mathbf{R}^*$, φ^*) in (5), applying the stationary-phase

method, [16] and symmetrizing the expression (5) with respect to the initial and final configurations, we obtain the final expression for the excitation amplitude (the three-body problem; μ is the reduced mass):

$$f_{nm}(p_i, p_f) = -\frac{\mu}{4\pi\hbar^2}\iint d\mathbf{R}^* \frac{d\varphi^*}{(2\pi)^3}\exp\left[\frac{i}{\hbar}(\Delta\mathbf{R}^* + \hbar\mathbf{k}\varphi^* + \Delta S_+)\right]\left[D_i W_n \exp\left(\frac{i}{\hbar}\Delta S_-\right) + D_f W_m \exp\left(-\frac{i}{\hbar}\Delta S_-\right)\right],$$

$$\Delta = \mathbf{p}_i - \mathbf{p}_f, \quad \mathbf{k} = \mathbf{n} - \mathbf{m}, \quad \mathbf{I}_{n,m} = \hbar(\mathbf{n}, \mathbf{m}+\delta)\ ^{1)}; \tag{8}$$

$$D_i = \left|\frac{\partial \mathbf{R}^*}{\partial \mathbf{R}'}\right|^{-1/2}\left|\frac{\partial \varphi^*}{\partial \varphi'}\right|^{-1/2}, \quad D_f = \left|\frac{\partial \mathbf{R}^*}{\partial \mathbf{R}}\right|^{-1/2}\left|\frac{\partial \varphi^*}{\partial \varphi}\right|^{-1/2},$$

$$\Delta S_\pm = 1/2(\Delta S_i \pm \Delta S_f), \quad \mathbf{I}_{\tilde{\nu}} = \hbar(\nu+\delta),$$

$$\Delta S_i = \int_{\mathbf{R}'}^{\mathbf{R}^*}(\tilde{\mathbf{p}} - \mathbf{p}_i)\,d\tilde{\mathbf{R}} + \hbar\int_{\varphi'}^{\varphi^*}(\tilde{\nu} - \mathbf{n})\,d\tilde{\varphi},$$

$$\Delta S_f = \int_{\mathbf{R}^*}^{\mathbf{R}}(\tilde{\mathbf{p}} - \mathbf{p}_f)\,d\tilde{\mathbf{R}} + \hbar\int_{\varphi^*}^{\varphi}(\tilde{\nu} - \mathbf{m})\,d\tilde{\varphi}. \tag{9}$$

In the formulas (8), (9) Δ and $\mathbf{k}$ are increments in the momentum and the quantum-number vector, while $D_{i,f}$ are the Jacobinas of the coordinate transformations.

The expressions (6) for the transition amplitude (the S matrix for $t - t' \to \infty$) and (8) for the T operator are suitable for the computation of transition probabilities and differential cross sections under quasiclassical conditions. Notice that (6) and (8) are expressions for the S and T matrices respectively. In a particular case (small angle scattering), the expression (8) reduces to the form of (6) and of a representation for the impact parameter. [15]

2. THE CLASSICAL PERTURBATION-THEORY METHOD

To compute the transition amplitudes with the aid of the formulas (6) and (8), it is necessary to know the classical-action increment ΔS, which can be found by means of perturbation theory. Let us, for definiteness, consider the excitation problem (the formula (8)), and formulate perturbation-theory methods in the case of fast ($t_c/T \ll 1$) and slow ($t_c/T \gg 1$) collisions.

The Hamiltonian function for the problem in the requisite variables has the form

$$H(\varphi, \mathbf{v}, \mathbf{R}, \mathbf{p}) = H_0(\mathbf{v}, \mathbf{p}) + \varepsilon W(\varphi, \mathbf{v}, \mathbf{R})$$
$$H_0 = \mathcal{H}_0(\mathbf{v}) + p^2/2\mu, \tag{10}$$

where $\mathcal{H}_0(\mathbf{v})$ is the Hamiltonian function for the target in the action variables $\mathbf{v}$ ($\mathbf{I} = \hbar(\mathbf{v} + \delta)$, φ varying in this case in a cube of edge length 2π) and ε is the smallness parameter.

Let us write down the canonical system of Hamilton's equations in the dimensionless time $\tau = \gamma^{-1}t$:

$$\dot{\varphi} = \gamma\frac{\partial \mathcal{H}_0(\mathbf{v})}{\partial \mathbf{v}} + \varepsilon\gamma\frac{\partial \overline{W}}{\partial \mathbf{v}}, \quad \dot{\mathbf{R}} = \gamma\frac{\mathbf{p}}{\mu},$$
$$\dot{\mathbf{v}} = -\varepsilon\gamma\frac{\partial W}{\partial \varphi}, \quad \dot{\mathbf{p}} = -\varepsilon\gamma\frac{\partial W}{\partial \mathbf{R}}. \tag{11}$$

In the case of fast collisions ($t_c/T \ll 1$, $t_c = R_0/V$ is the collision time, $T = \nu_0^{-1}$ is the characteristic period of the internal motions), let us set $\gamma = t_c$. We then have the dimensionless small parameters $\gamma\nu_0 \ll 1$ and $\varepsilon\gamma/\hbar \ll 1$ ($\nu_0 \sim \partial\mathcal{H}_0(\mathbf{v})/\partial\mathbf{v}$, $\gamma p/R_0\mu \sim \gamma V/R_0 \sim 1$).

In the case of slow collisions ($t_c/T \gg 1$), let us set $\gamma = T$ and obtain as the small parameters $\gamma V/R_0 \ll 1$ and $\varepsilon\gamma/\hbar \ll 1$; $\gamma\nu_0 \sim 1$. In both cases we have the small parameter $\varepsilon\gamma$ ($\hbar = 1$) in front of the perturbation[2)] when the relative motion is fast or slow. However, for slow collisions, we should regard φ ($\gamma\nu_0 \sim 1$) as the "fast" variable, while for fast collisions $\mathbf{R}$ ($\gamma V/R_0 \sim 1$) should be regarded as the "fast" variable. Such a separation of the motions into "fast" and "slow" motions allows us to apply in canonical systems a fairly general perturbation-theory method, [17] which is constructed on the basis of the principle of averaging of Eqs. (11) over the "fast" variable. As applied to the problems of the theory of collisions, this method was developed in Ref. 18. In particular, if the Hamiltonian H has with respect to the "fast" variable an average value equal to zero (fast collisions), then it coincides with the canonical theory of perturbations. On the other hand, for slow collisions H has an average value $\overline{H}$ and a periodic part $\tilde{H}$, as a result of which the expansion in powers of the small parameter is constructed differently. Let us give the principal expressions of the perturbation theory that are necessary for the computation of the increments in the action in the case of fast and slow collisions.

A. For greater clarity in the case of fast collisions ($\varepsilon\gamma/\hbar \ll 1$), we shall proceed from the standard version of the canonical perturbation theory for the "eikonalized" Hamilton–Jacobi equation, which can be written in the form

$$\mathcal{H}_0\left(\frac{\partial S}{\partial \varphi}\right) + \mathbf{V}_l\frac{\partial S}{\partial \mathbf{R}} + \varepsilon W\left(\frac{\partial S}{\partial \varphi}, \varphi, \mathbf{R}\right) = \mathscr{E} + \frac{p_l^2}{2\mu}. \tag{12}$$

In this equation $\mathscr{E}$ denotes the internal energy of the target, and we have made the approximating substitution $p^2/2\mu \approx -p_l^2/2\mu + \mathbf{V}_l\mathbf{p}$, $\mathbf{V}_l = \mathbf{p}_l/\mu$, where $\mathbf{p}_l$ is the relative-momentum value which is approximately conserved along the segment l of the path, and which we shall choose later.

Let us seek the solution to (12) in the form of the expansion (we formally assume ε to be a small parameter in both cases)

$$S = \sum_{p=0}^{\infty} S_p(\varphi, \alpha, \mathbf{R}, \beta)\varepsilon^p, \tag{13}$$

and let us, in accordance with the condition of the problem, take as the arbitrary constants α and β (generalized momenta) along the segment l of the path, the corresponding ν_l and $\mathbf{p}_l$ values determined below from the condition of the problem. Evidently, we have in this case

$$\alpha = \frac{\partial S_0}{\partial \varphi} = \nu_l, \quad \beta = \frac{\partial S_0}{\partial \mathbf{R}} = \mathbf{p}_l. \tag{14}$$

Further, substituting (13) into (12), we obtain a system of equations for the determination of S_p:

$$S_0 = \mathbf{p}_l\mathbf{R} + \nu_l\varphi, \quad \frac{\partial \mathcal{H}_0(\nu_l)}{\partial \nu_l}\frac{\partial S_p}{\partial \varphi} + \mathbf{V}_l\frac{\partial S_p}{\partial \mathbf{R}} = -K_p(\varphi, \mathbf{v}, \mathbf{R}, \mathbf{p}_l), \tag{15}$$

where

$$K_1(\xi, Z_l)=W(\xi, Z_l), \quad K_2(\xi, Z_l) = \{S_1, W\}+{}^1/_2\{S_1\{S_1, \mathscr{H}_0\}\}, \tag{16}$$

and $\{X, Y\}$ denotes the classical Poisson brackets with respect to the variables ξ and Z_l:

$$\{X, Y\}=\frac{\partial X}{\partial \xi}\frac{\partial Y}{\partial Z_l}-\frac{\partial X}{\partial Z_l}\frac{\partial Y}{\partial \xi}. \tag{17}$$

The Eqs. (15) for $p \geq 1$ have a simple solution in the form of an integral over the unperturbed path along the segment l:

$$S_p=-\int_{-\infty}^{t} K_p(\varphi(\tau), \mathbf{v}_l, \mathbf{R}(\tau), \mathbf{p}_l)\,d\tau, \quad \varphi(\tau)=\varphi_l+\mathbf{v}_l\tau, \tag{18}$$

$$\mathbf{R}(\tau)=\mathbf{R}_l+\mathbf{V}_l\tau;$$

$$\mathbf{v}_l=\partial\mathscr{H}_0(\mathbf{v}_l)/\partial\mathbf{v}_l. \tag{19}$$

Determining S_p, we find the expansion in powers of ε of the equations of the precise path along the segment l:

$$\mathbf{v}=\partial S/\partial\varphi=\mathbf{v}_l+\varepsilon\mathbf{v}_l^{(1)}+\varepsilon^2\mathbf{v}_l^{(2)}+\ldots,$$

$$\mathbf{p}=\partial S/\partial\mathbf{R}=\mathbf{p}_l+\varepsilon\mathbf{p}_l^{(1)}+\varepsilon^2\mathbf{p}_l^{(2)}+\ldots, \tag{20}$$

and along with it, from (8), the well-known formulas of collision theory (the Born and the eikonal formulas) in the action-angle variables with subsequent corrections. In particular, in first-order canonical perturbation theory, we obtain the eikonal formula (see Ref. 11) in the action-angle variables with a correction for the internal motion of the target:

$$f_{nm}(\mathbf{p}_i, \mathbf{p}_f)=-\frac{\mu}{2\pi\hbar^2}\iint d\mathbf{R}\frac{d\varphi}{(2\pi)^3}W_a\exp\left[\frac{i}{\hbar}(\Delta\mathbf{R}+\hbar\mathbf{k}\varphi+\delta_+)\right]; \tag{21}$$

$$W_a=\frac{1}{2}[W(\mathbf{n}, \varphi, \mathbf{R})+W(\mathbf{m}, \varphi, \mathbf{R})], \quad \mathbf{v}_{nm}=\frac{\partial\mathscr{H}_0(\mathbf{n}, \mathbf{m})}{\partial(\mathbf{n}, \mathbf{m})},$$

$$\mathbf{V}_{i,f}=\frac{\mathbf{p}_{i,f}}{m_1},$$

$$\delta_+(\mathbf{R}, \varphi)=-\frac{1}{2}\int_0^\infty W(\mathbf{n}, \varphi-t\mathbf{v}_n, \mathbf{R}-\mathbf{V}_i t)\,dt \tag{22}$$

$$-\frac{1}{2}\int_0^\infty W(\mathbf{m}, \varphi+t\mathbf{v}_m, \mathbf{R}+\mathbf{V}_f t)\,dt.$$

B. In the case of slow collisions ($\gamma V/R_0 \ll 1$), the periodic time function $\varphi(\tau)$ is the "fast" variable, and therefore here, instead of the canonical theory of perturbations, we should apply the method of asymptotic averaging.[18]

In applying this method to the canonically conjugate variables φ and $\mathbf{v}$, we shall regard the variables R and p as parameters, the set of which we shall denote by the single letter λ. In the analysis below we assume $\lambda(t)$ to be a slowly varying function of the time. According to the method of asymptotic averaging, as applied to our problem,[18] we should seek such canonical transformation of the variables, φ, $\mathbf{v}-\varphi_*$, $\mathbf{v}_*$, in which $H(\varphi, \mathbf{v}, \lambda)$ goes over into a Hamiltonian function, $\overline{H}(\mathbf{v}_*, \lambda)$, that depends only on $\mathbf{v}_*$. As can be shown,[18] the expression for $\overline{H}$ has the form

$$\overline{H}(\mathbf{v}_*, \lambda)=H_0(\mathbf{v}_*, \lambda)+\varepsilon\overline{W}(\mathbf{v}_*, \lambda)+\varepsilon^2[\overline{\{W, \hat{W}\}} + {}^1/_2\overline{\{\hat{W}\{\hat{W}, H_0\}\}}]+\ldots, \tag{23}$$

where

$$\overline{X}(\mathbf{v}_*, \lambda)=\lim_{T\to\infty}\frac{1}{T}\int_0^\tau X[\varphi(\tau'), \mathbf{v}_*, \tau', \lambda]\,d\tau',$$

$$\hat{X}(\varphi, \mathbf{v}_*, \tau, \lambda)=\int_0^\tau\{X[\varphi(\tau'), \mathbf{v}_*, \tau', \lambda]-\overline{X}\}\,d\tau'.$$

The action function for the general nonstationary case can then be written in the form of a series in powers of ε:

$$S(\varphi, \mathbf{v}_*, \tau, \lambda)=\int^{\varphi}\mathbf{v}_*\,d\varphi+\int\overline{H}\,d\tau'+\sum_{p=1}^{\infty}\varepsilon^p\overline{K}_p(\varphi, \mathbf{v}_*, \tau, \lambda), \tag{24}$$

where the K_p are defined by the formulas (16).

For the stationary problem of scattering of an atom on a target, we identify, after carrying out the computations, τ with t, make the substitution $\lambda(t)-\mathbf{R}(t)$, $\mathbf{p}(t)$, and carry on the analysis as before. In this case we add to the action function (24) the term $\int^R\mathbf{p}\,d\mathbf{R}'$, which is computed over the paths with the Hamiltonian $\overline{H}$.

Let us note, not dwelling for lack of space on details, the distinctive features of the method of asymptotic averaging. For $\overline{K}_p=0$ it coincides with the canonical perturbation theory, differing from it in the case when $\overline{K}_p\neq 0$.

The method is applicable to the case of nonstationary perturbations $W(t)$; in the stationary case, however, the expansion (23) coincides with the Born expansion,[12] which was used in the old quantum mechanics to determine corrections to the energy.

3. THE AMPLITUDE OF THE INELASTIC SCATTERING OF A CHARGED PARTICLE ON A HYDROGEN ATOM

As the first example, let us calculate the amplitude of the inelastic scattering $(p, e)+H(n, l, m)-(p, e)+H(n', l', m')$ at high energies. Interest to this reaction is due to the fact that the Glauber amplitudes diverge at zero angles in the case of the Coulomb potentials,[2] and the procedure for their regularization is important for applications of the eikonal method in the case of processes in which charged particles participate.

To solve this problem, we shall proceed from the formulas (21) and (22), which take screening in the eikonal phase into account. Let us focus our attention on small-angle scattering and small changes in the quantum-number vector $\mathbf{k}$. We can limit ourselves to the dipole approximation for the potential

$$W\approx -ee'\mathbf{r}\mathbf{R}/R^3, \quad e'=\pm e, \tag{25}$$

and use in place of the quantities $\mathbf{n}$, ν_n and $\mathbf{m}$, ν_m the corresponding mean values $\mathbf{n}_a$, ν_a. Then in the expression (21) we can carry out the integration over the coordinate y ($R=(\rho^2+y^2)^{1/2}$, see Fig. 1) in much the same way as is done in the eikonal method[14,15] and obtain a generalization of the Glauber formula with allowance for the internal motion along an ellipse with frequency ν_{1a} (see Fig. 1; $\nu_{2a}=\nu_{3a}=0$, $\varphi=(\varphi_1, \varphi_2, \varphi_3)$, $\mathbf{k}=(k_1, k_2, k_3)$, $\mathscr{H}=p/\hbar$):

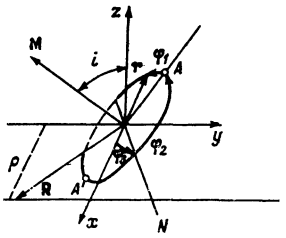

FIG. 1. Bound orbit (the NA plane) and the trajectory of the relative motion (the xy plane). N) line of nodes, A) perihelion; φ_1, φ_2, φ_3) angular variables (elements of the orbit in units of $\hbar$); $\cos i \equiv v_3/v_2$; $v_1 \equiv n_r + l + 1$, $v_2 \equiv l$, $v_3 \equiv M$ are the components of the quantum-number vector.

$$f_{nm}(\theta) = -\frac{i\varkappa}{(2\pi)^3}\int_0^{\infty}\rho d\rho J_0(\varkappa\rho\theta)\int_0^{2\pi}d\varphi\left[\exp\left(i\mathbf{k}\varphi+\frac{2i}{\hbar}\delta\right)-\delta_{nm}\right]. \quad (26)$$

$$\delta(\varphi,\rho) = -\frac{1}{2V}\int_{-\infty}^{+\infty} W\left(\mathbf{n}_a, \varphi_1+\frac{y'}{V}\nu_{1a}, \varphi_2, \varphi_3, \rho, y'\right)dy'. \quad (27)$$

In writing down this formula we also made the reasonable assumption that the various orientations of the ellipse in space are distributed with weight $\exp(i\varphi_2 n_2 + i\varphi_3 n_3)$. This assumption is justified when we take into account additional perturbations (the relativistic splitting of the levels, the introduction of perturbed stationary states, etc.) leading to the removal of the degeneracy ($\nu_2 \neq \nu_3 \neq 0$) and the slow precession of the elements of the orbit. The meaning of all the angles and the other quantities is clear from Fig. 1, from which, with allowance for (25), we can derive an explicit expression for the eikonal phase in the requisite variables:

$$\delta = \frac{ee'a_a}{V^2}\left\{-\frac{3}{2}\frac{V\varepsilon_a}{\rho}(\cos^2\varphi_3+\cos^2 i_a\sin^2\varphi_3)^{1/2}\cos(\varphi_2+\lambda_2)\right.$$
$$+\nu_{1a}D_1\left[\left(K_1\left(\frac{\nu_{1a}}{V}\rho\right)+K_0\left(\frac{\nu_{1a}}{V}\rho\right)\cos i_a\right)\cos\varphi_3\cos(\varphi_1+\varphi_2)\right.$$
$$\left.\left.-\left(K_1\left(\frac{\nu_{1a}}{V}\rho\right)\cos i_a+K_0\left(\frac{\nu_{1a}}{V}\rho\right)\right)\sin\varphi_3\sin(\varphi_1+\varphi_2)\right]\right\}, \quad (28)$$

where $D_1 = J_0(\varepsilon_a) + J_1(\varepsilon_a)$, $\nu_{1a} = me^4/\hbar^3 n_{1a}^3$ is the angular frequency, $a_a = n_{1a}^2\hbar^2/me^2$ is the major semiaxis of the ellipse, $\varepsilon_a = (1 - n_{2a}/n_{1a})^{1/2}$ is the eccentricity, $\lambda_2(\varphi_3) = \tan^{-1}(\cos i_a \tan\varphi_3)$, $\cos i_a = n_{3a}/n_{2a}$, and the $J_{0,1}$ and $K_{0,1}$ are Bessel and Macdonald functions. Under the quantum numbers (n_1, n_2, n_3) we understand respectively $(n \equiv n_r + l + 1,\ l,\ m)$; the index a designates the average values of the elements of the orbit. The expression (26) can, with allowance for (28), be written in the form (γ_0 is the phase, which we do not write out):

$$f_{nm}(\theta) = e^{i\gamma_0}\varkappa\int_0^{\infty}\rho\, d\rho\, J_0(\varkappa\theta\rho)$$
$$\times\left\{\int_0^{2\pi}\frac{d\varphi_3}{2\pi}\exp[ik_3\varphi_3 - i(\lambda_1 k_1+\lambda_2(k_2-k_1))]J_{k_1}(Q)J_{k_2-k_1}(q)-\delta_{mn}\right\}. \quad (29)$$

Here we have introduced the notation

$$Q(\varphi_3,\rho) = \frac{2ee'\nu_{1a}a_a}{V^2\hbar}D_1\{(K_1+K_0\cos i_a)^2\cos^2\varphi_3+(K_1\cos i_a+K_0)^2\sin^2\varphi_3\}^{1/2},$$
$$q(\varphi_3,\rho) = \frac{3ee'a_a}{V\hbar\rho}\varepsilon_a(\cos^2\varphi_3+\cos^2 i_a\sin^2\varphi_3)^{1/2},$$
$$\lambda_1(\varphi_3) = \operatorname{arc\,tg}\left(\frac{K_1\cos i_a+K_0}{K_1+K_0\cos i_a}\operatorname{tg}\varphi_3\right).$$

As is easy to see, the expression (29) is finite at $\theta = 0$. In particular, for the amplitude of the zero-angle elastic scattering in the ground state we obtain

$$f_{1s,1s}(0) = -i\varkappa\int_0^{\infty}\rho\, d\rho\left\{\int_0^{2\pi}\frac{d\varphi_3}{2\pi}J_0[2\eta^2(K_1^2(\eta\rho)\cos^2\varphi_3+K_0^2(\eta\rho)\sin^2\varphi_3)^{1/2}]-1\right\} \quad (30)$$

Using the optical theorem, we obtain from this the total excitation cross section:

$$\sigma = 2\eta^3 K_1(\eta)K_0(\eta)(\pi a_0^2), \qquad \eta = e^2/\hbar V. \quad (31)$$

From (31) for low velocities ($V \leq 10^8$ cm/sec) we have, using the asymptotic forms of the Macdonald functions, the following expression:

$$\sigma = \pi\eta^2(\pi a_0^2), \quad (32)$$

while for high velocities ($V \gg 10^8$ cm/sec) we have

$$\sigma = 2\eta^2\left(\ln\frac{2\hbar V}{e^2} - C\right)(\pi a_0^2), \quad (33)$$

where $C = 0.5772$ is the Euler constant.

In Fig. 2 we show the correlation of our computed differential cross section for the $1s \to 2s$, p excitation with the data given in Refs. 19 and 20. As can be seen, the correction for the internal motion is important at lower energies. Thus, the considered correction leads to a significant change in the angular distribution, contrary to Jochain's assertion[21] that the difference between the various modifications of the Glauber formula is insignificant.

4. TRANSITIONS BETWEEN HIGHLY-EXCITED STATES IN COLLISIONS OF TWO HYDROGEN ATOMS

Let us consider the process of excitation of the highlying states in the reaction $H(1s)+H(n, l, m) \to H(1s)+H(n', l', m')$, and use in computing the transition probabilities the model of an outer electron in the variable field of the ion H_2^+. In this case the variable field is produced both as a result of the continual transitions of the core electron from one nucleus to another (the fast field) and as a result of the relative nuclear motion, which we shall assume to be classical. The Schrödinger

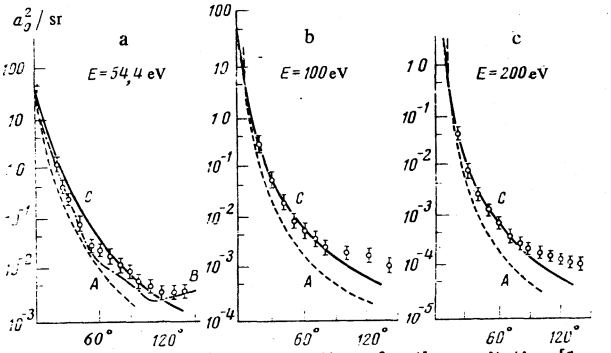

FIG. 2. Differential cross sections for the excitation [$1s \to 2s + 2p$] of the hydrogen atom by electron impact: A) the Glauber approximation[2,19]; B) close-coupling method[20]; C) computed from the formula (29), $a_a = \nu_{1a} = 1$ a.u.; the points are experimental points.[19]

equation for the valence electron r_2 in the variable field $W(r_2, t)$ has the form

$$i\hbar\frac{\partial\Phi}{\partial t}=\left[-\frac{\hbar^2}{2m}\nabla_{r_2}^2-\frac{e^2}{r_2}+W(r_2,t)\right]\Phi, \qquad (34)$$

$$\Phi(r_2,t)\xrightarrow[t\to-\infty]{}\varphi_n(r_2)e^{-iE_nt/\hbar},$$

and for the potential $W(r_2, t)$ under the condition

$$r_2^*\gg r_1^*. \qquad (35)$$

($r_{1,2}^*$ are the mean radii of the orbits of the core and valence electrons) we can write, up to the quadrupole terms, the expression

$$W(r_2,t)\approx\left(e^2\frac{X_\alpha x_\alpha}{r_2^2}-\frac{e^2}{2}D_{\alpha\beta}\frac{x_\alpha x_\beta}{r_2^5}\right)\sin^2\left(\frac{1}{2\hbar}\int_0^t\Delta(t')dt'\right). \qquad (36)$$

In the formula (36), the x_α are the components of the radius vector $\mathbf{r}_2$, the X_α are the components of the radius vector R, and Δ is the difference between the terms of the symmetric and antisymmetric states for the system H_2^+. The system of coordinates has been chosen as follows: the origin is located at the center of the $H(n, l, m)$ atom, the $\hat{x}_2$ axis is directed along the initial relative velocity (for simplicity, the motion of the nuclei is assumed to be rectilinear), and $\hat{x}_1$ is directed along the radius vector of the point of closest approach, so that the vectors $\hat{x}_1$, $\hat{x}_2$ define the scattering plane. In computing the transition probability $P_{nm}(\rho)=|a_{nm}(t', t)|^2\times(t-t'\to\infty)$, we proceed from the expression (6) and compute $\Delta S_\pm$, $D_{i,f}$ in first-order perturbation theory in the case of fast internal motions (§2, Subsec. B). The necessary computations in the requisite variables have already been carried out by us[18]; therefore, we substitute them at once into the expression (6). Notice only that, in contrast to the case of fast collisions, the degeneracy of the levels is now removed even in first-order perturbation theory, and $D_{i,f}\neq1$. The final expression for $P_{nm}(\rho)$ in atomic units has the form

$$P_{nm}(\rho)=J_{k_1}^2\left[\frac{\rho}{2}\left(\frac{n_3}{n_1n_2}-\frac{m_3}{m_1m_2}\right)\right]\left|\int_0^t dq_3\,e^{iQ}D\right|^2. \qquad (37)$$

In this formula (n_1, n_2, n_3) and (m_1, m_2, m_3) are sets of three quantum numbers in the initial and final states $(n_1=n,\ n_2=l,\ n_3=m,\ m_1=n',\ m_2=l',\ m_3=m')$,

$$\Omega=\frac{n_2+m_2}{2}\left\{\arccos q_3-\sin i\,\mathrm{arctg}\left[\frac{q_3\sin i}{(1-q_3^2)^{1/2}}\right]\right\}, \qquad (38)$$

$$D=\frac{2\cos i\sin i}{\pi(1-q_3^2\cos^2 i)(1-q_3^2)^{1/2}},\quad \cos i=\frac{n_3+m_3}{n_2+m_2},\quad k_1=|m_1-n_1|.$$

The expression (37) has been derived under the limitations on n_1 and m_1 that follow from (35), as well as under the following limitations on the impact parameter and on the relative velocity V (in atomic units):

$$\rho\leqslant\rho_0=\ln(4/3V),\qquad V<1/n_1. \qquad (39)$$

Assuming that the dominant contribution to the cross section is made by the parameters satisfying the condition (39), we obtain an approximate expression for the total transition cross section:

$$\sigma_{nm}=\frac{\rho_0^2\cos^2 i}{2}\left\{[J_{k_1}'(a\rho_0)]^2+\left(1-\frac{k_1^2}{a^2\rho_0^2}\right)[J_{k_1}(a\rho_0)]^2\right\},$$

$$a=\left(\frac{n_3}{n_1n_2}-\frac{m_3}{m_1m_2}\right).\quad \cos i=\frac{m_3+n_3}{m_2+n_2}. \qquad (40)$$

Unfortunately, we do not know of any theoretical or experimental data, a comparison with which would enable us to judge the accuracy of the formulas (37) and (40).

5. THE DIFFERENTIAL CROSS SECTIONS FOR THE ROTATIONAL TRANSITIONS OCCURRING IN THE $Li^+ + H_2$ COLLISION

It is of interest to compute the cross sections for rotational excitation in the $Li^+ + H_2$ system, which is the most fully experimentally investigated system at present. We shall consider only the rotation of the H_2 cule, and also take the analytic expression for the Li^+–H_2 interaction potential for the rotational transitions from Ref. 22. The Hamiltonian function has the form (in the atomic system of units)

$$H=\frac{p^2}{2\mu}+2\pi B_e j(j+1)-\frac{0{,}69}{R^3}-\frac{2{,}79}{R^4}+\left(\frac{0{,}46}{R^3}-\frac{0{,}60}{R^4}\right)\cos^2\gamma. \qquad (41)$$

Here j is the orbital moment, B_e is the rotational constant, γ is the angle between the vectors R and $\mathbf{r}$, μ is the reduced mass of the $Li^+ + H_2$ system, and $\mathbf{p}$ is the relative momentum. For molecules with small moments of inertia in the region of energies up to 1 eV, the condition $\omega_j t_c\gg1$ is fulfilled, i.e., the angular variable φ_j, which is conjugate to the moment j, is a "fast" variable, while the remaining variables R, $\mathbf{p}$, j, m_j, and φ_{m_j} are 'slow" variables (φ_{m_j} is the angular variable conjugate to m_j). The computation of all the quantities ($\bar{H}$ and S) in this case is completely similar to the computation of these quantities in the case of two hydrogen atoms, as a result of which we obtain (in first order in ε)

$$\bar{H}=H_0+\varepsilon\bar{V}=\frac{p^2}{2\mu}-\frac{0{,}69}{R^3}-\frac{2.79}{R^4}+2\pi B_e j(j+1)+\frac{1}{2}\left(\frac{0.46}{R^3}-\frac{0.60}{R^4}\right)\cos i\,(1+q_{m_j}^2\,\mathrm{tg}^2\,i). \qquad (42)$$

$$\Delta S=\Delta S_y+\Delta S_j+\Delta S_{m_j}=\int_R\mathbf{p}\,d\mathbf{R}+j\varphi_j+\frac{1}{\omega_j}\left(\frac{0.46}{R^3}-\frac{0.60}{R^4}\right)\times\sin^2\varphi_j+\sin i\,\mathrm{arctg}\left(\frac{q_{m_j}\sin i}{(1-q_{m_j}^2)^{1/2}}\right)-\sin^2 i\,\arcsin q_{m_j}. \qquad (43)$$

where

$$\sin^2 i=1-m_j^2/j^2,\quad \cos i=m_j/j,\quad \omega_j=2\pi B_e(2j+1),$$
$$q_{m_j}=\cos\varphi_{m_j}/\cos i.$$

Substituting (43) into (8), and separating out the elastic-scattering amplitude within the framework of the sta-

TABLE I. Relative differential cross sections for the rotational transitions $0\to2$ and $1\to3$ in Li^+ scattering on ortho- and parahydrogen H_2 (in a 3:1 ratio) for a relative-motion energy $E=0.60$ eV.

θ, deg	$I(0\to0+1\to1):I(0\to2):I(1\to3)$		
	Experiment[23]	Computed by the [23] Monte-Carlo method	Computed from formula[44]
14	0.88:0.06:0.06	0.80:0.08:0.12	0.84:0.08:0.06
20	–	0.66:0.12:0.22	0.82:0.09:0.09
23	0.74:0.10:0.16	–	0.77:0.10:0.12
25	–	0.61:0.11:0.28	0.76:0.10:0.14
32	0.76:0.10:0.14	0.61:0.16:0.23	0.75:0.10:0.14

tionary-phase method with respect to R, in much the same way as was done in Ref. 15, we have in the "finite-coordinate" representation

$$f_{nm}(\mathbf{p}_i, \mathbf{p}_f) = f_v(\mathbf{p}_i, \mathbf{p}_f) J_{k_j/2} \left[\frac{V_e(R_0)}{4\omega_j \hbar} \right] \int_0^t dq_{m_j} \left| \frac{\partial m_j}{\partial m_{j0}} \right|^{1/2} \exp\left(\frac{i}{\hbar} \Delta S_{m_j} \right) \quad (44)$$

where R_0 is the point of closest approach,

$$f_v = \frac{\mu}{2\pi} \int dR\, V_e(R) \exp\left[\frac{i}{\hbar} \Delta S_v(\theta, \mathbf{p}, \mathbf{R}) \right], \quad V_e(R) = -\frac{0{,}46}{R^3} - \frac{3{,}09}{R^4},$$
$$\left| \frac{\partial m_j}{\partial m_{j0}} \right| = \frac{4 \cos^2 i \sin i}{\pi^2 (1 - \cos^2 i\, q_{m_j}^2)(1 - q_{m_j}^2)^{1/2}}, \quad k_j = |j - j'|. \quad (45)$$

The specific cross-section magnitudes for the $Li^+ + H_2$ system were next computed from the formula

$$d\sigma_{j' \to j}/d\Omega = |f_{j'j}(\theta)|^2.$$

Relative cross-section values are given in Table I and compared with experiment and the results of numerical computations of other authors.[23] As can be seen from the comparison, the formula (44) guarantees a good computational accuracy for small-angle scattering. Notice that the formula (44) is not tied with a specific system, and can be used to calculate the rotational transitions in the rigid-rotator and anisotropic-interaction-potential approximation. In Table I we give the ratios of the elastic-scattering intensity to the rotational-excitation intensities for para- and orthohydrogen $[I(0 \to 0+1 \to 1) : I(0 \to 2) : I(1 \to 3)]$. Under the intensity $I(0 \to 0+1 \to 1)$ we understand the expression

$$\left[\frac{1}{4} \frac{d\sigma}{d\Omega}(0 \to 0) + \frac{3}{4} \frac{d\sigma}{d\Omega}(1 \to 1) \right] \left[\frac{1}{4} \frac{d\sigma}{d\Omega}(0 \to 0) + \frac{3}{4} \frac{d\sigma}{d\Omega}(1 \to 1) + \frac{1}{4} \frac{d\sigma}{d\Omega}(0 \to 2) + \frac{3}{4} \frac{d\sigma}{d\Omega}(1 \to 3) \right]^{-1}$$

The intensities $I(0 \to 2)$ and $I(1 \to 3)$ are computed in much the same way.

[1)]The Bohr–Sommerfeld condition, which relates the action variable I with the quantum-number vectors **n** and **m**; **δ** is a constant vector.

[2)]Naturally, the perturbation can be weak on account of the single parameter ε.

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