show up in various dispersed conditions; fine, almost atomic, dispersion, is the cause of green luminescence and also of after glowing, because of the creation of structures connected with the occurrence of the "trap sites" of electrons. When particle of copper grows up to the colloidal size, the luminescent properties of copper disappear. The degree of dispersion of copper metal can change under influence of the secondary action of the chlorides. Thus, the fluxes can play a great but auxiliary role.

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The Theory of Scattering in the Semi-Classical Approximation

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A method is given for finding the wave function and the Green's function for a three-dimensional problem in the semi-classical approximation. The idea of the method is illustrated by the problem of reflection from a barrier.

1. INTRODUCTION

IN scattering problems the semi-classical approximation is usually applied to the calculation of the phase shifts corresponding to the different angular momenta of the particle. This method is applied only in the case of a central field.

In the present work it is shown that the wave function can be found without the assumption of the central character of the potential field, if the trajectories of the classical problem are known.

As is well known, the semi-classical approximation, which has been thoroughly studied in the one-dimensional case, does not give the exact solution, but an asymptotic series in the semi-classical parameter ξ($\xi = \lambda\!\!\!^{-} / l$ where $\lambda\!\!\!^{-}$ is the wave-length of the particle, l, is a length characterizing the variation of the potential). Quantum effects, which decrease exponentially with diminishing ξ, cannot be determined in any approximation of this asymptotic series, because the error of the asymptotic representation exceeds the effect sought.

Let us consider, for example, the problem of the calculation of the reflection coefficient from a potential barrier V, when the conditions of the semi-classical approximation are fulfilled in the entire space (i.e., the kinetic energy is nowhere reduced to zero). It is not difficult to see that neither the first nor the succeeding approximations in ξ contain terms corresponding to the reflected wave. Analogous questions arise in the three-dimensional problem also. For example, in the case in which the deflection into large angles is forbidden in classical mechanics, the scattering into these angles decreases exponentially with diminishing ξ, and cannot be found with the aid of an asymptotic expansion in ξ.

In the present work a method is given for improving the semi-classical approximation, which enables us to find the solution of the above-mentioned problems. This method consists of the following: the wave function of the problem is written in the form $\psi = \psi_0 + \psi_1$, whereby ψ_0 is the ordinary semi-classical solution; for ψ_1 an inhomogeneous equation is obtained, the solution of which is found by the use of the Green's function. In this work it is shown how one can obtain an approximate Green's function, if the trajectories of the classical problem is known.

2. ONE-DIMENSIONAL PROBLEM

1. It is required to find the solution of the Schrödinger equation

$$\psi'' + k^2(x)\psi = 0, \qquad (1)$$
$$k^2 = 2[E - V(x)], \quad m = h = 1,$$

describing the reflection from a potential barrier $V(x)$ under conditions such that the condition for the application of the semi-classical approximation is satisfied at all points ($d\hbar/dx \ll 1$).

The solution of the problem can be sought in the form

$$\psi_0 = Ae^{iS}. \tag{2}$$

The function S satisfies the equation

$$S'^2 - (A''/A) = k^2; \quad A = \sqrt{k_0/S'}. \tag{3}$$

Equation(3) is an exact consequence of Eqs. (1) and (2). Considering A''/A a small quantity and finding S by the method of successive approximations, we find (for particles incident from the left)

$$\varphi_0 = \sqrt{k_0/k}\, \exp\left\{i\int^x k dx\right\} \tag{4}$$

$$\times \quad \{1 + \xi F_1(x) + \xi^2 F_2(x) + \ldots\},$$

where $\xi = \hbar/l$ is the semi-classical parameter.

The solution (4) as $x \to -\infty$ does not contain terms of the form e^{-ik_0x} in any approximation in ξ, which corresponds to the absence of the reflected wave. In order to determine the coefficient of reflection we put $\psi = \psi_0 + \psi_1$, where

$$\psi_0 = Ae^{iS}, \quad A = \sqrt{k_0/S'}, S = \int^x k dx.$$

Substituting these expressions in Eq. (1), we obtain

$$\psi_1'' + k^2(x)\psi_1 = -A''e^{iS} = -f(x). \tag{5}$$

If we know two linearly independent solutions ϕ_1 and ϕ_2 of Eq. (5) without the right-hand side, then

$$\psi_1(x) = \frac{1}{\Delta}\left\{\varphi_1(x)\int_{-\infty}^{x}\varphi_2(x')f(x')dx'\right. \tag{6}$$

$$\left. + \varphi_2(x)\int_x^{\infty}\varphi_1(x')f(x')dx'\right\},$$

where Δ is the Wronskian determinant: $\Delta = \phi_1\phi_2' - \phi_1'\phi_2$. We assume that $\phi_1 \to e^{ik_0x}$ as $x \to +\infty$, $\phi_2 \to e^{-ik_0x}$ as $x \to -\infty$; then the wave function possesses the required asymptotic form:

$$\psi = \psi_0 + \psi_1 = e^{ik_0x}$$

$$+ \frac{e^{-ikx}}{\Delta}\int_{-\infty}^{+\infty}\varphi_1 f dx' \quad (x \to -\infty),$$

$$\psi \to e^{ik_0x}\left[1 + \frac{1}{\Delta}\int_{-\infty}^{+\infty}\varphi_2 f dx\right] \quad (x \to +\infty).$$

The coefficient of reflection is given by the formula:

$$R = \left|\frac{1}{\Delta}\int_{-\infty}^{+\infty}\varphi_1 f dx\right|^2 \tag{7}$$

Since Δ = const, we shall calculate Δ as $x \to \infty$. As $x \to \infty$ the function ϕ_1 takes the form e^{ik_0x}, while the function ϕ_2, on account of the smallness of the coefficient of reflection, is approximately given by

$$\varphi_2 \to e^{-ik_0x + i\alpha}.$$

From this it follows that $|\Delta| = 2k_0$.

For calculation of the integral in Eq. (7) one can use for ϕ_1 the semi-classical expression in first approximation. It is easy to see that an improvement in the precision of ϕ_1 leads to small corrections in R (of the order of ξ). Therefore the expression for R has the form

$$R = \frac{1}{4k_0^2}\left|\int_{-\infty}^{+\infty} A''Ae^{2iS}dx\right|^2. \tag{8}$$

2. For calculation of the integral in Eq. (8) it is convenient to transform to integration in the complex plane. First of all we make the following transformation:

$$I = \int_{-\infty}^{+\infty} A''Ae^{2iS}dx = A'Ae^{2iS}\Big|_{-\infty}^{+\infty}$$

$$\int_{-\infty}^{+\infty}(A'A\,2iS' + A'^2)e^{2iS}dx.$$

The first term reduces to zero, since $V' \to 0$ as $x \to \pm\infty$. The second term under the integral sign is small in comparison with the first, on account of the semi-classical conditions of the problem. Expressing A in terms of S', we get:

$$I \approx ik_0 \int_{-\infty}^{+\infty} \frac{S''}{S'} e^{2iS} dx = \frac{ik_0}{2} \int_{-\infty}^{+\infty} \frac{V'}{E-V} e^{2iS} dx. \quad (9)$$

It is convenient to carry out the integration of Eq. (9) in the complex plane. The integral along the infinite semicircle in the upper half-plane is equal to zero, since as $x \to \infty$, $S(x) \to +kx$. In this way the problem is reduced to the investigation of the singular points of the integrand of Eq. (9).

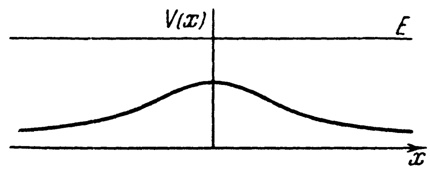

Fig. 1

3. THE THREE-DIMENSIONAL PROBLEM

1. Let us find an expression for the wave-function in the semi-classical approximation in the three-dimensional case. In the wave equation

$$\Delta\psi + 2(E - V(\mathbf{r}))\psi = 0$$

let us make the substitution $\psi = e^{iS}$, where A and S are real functions. From the requirement of the vanishing of the imaginary part, we obtain $\mathrm{div}(A^2 \nabla S) = 0$, or

$$\int A^2 \frac{\partial S}{\partial n} d\sigma = 0, \quad (10)$$

where the integration is carried out over a closed surface. Setting the real part equal to zero, we find

$$(\Delta A/A) - (\nabla S)^2 + k^2 = 0, \ k^2 = 2(E - V).$$

The condition for the application of the semi-classical approximation implies the smallness of the first term $\Delta A/A$. Neglecting this term, we obtain for S the Hamilton-Jacobi equation of classical mechanics

$$(\nabla S)^2 = 2(E - V).$$

If the trajectories are known for this classical problem, then

$$S(\mathbf{r}) = \int^{\mathbf{r}} k dl, \quad (11)$$

where $k = \sqrt{2(E-V)}$ and the integration is carried out along the classical trajectory.

At the end of this work we shall need the semi classical expression for the Green's function $G(\mathbf{r}, \mathbf{r}')$. The semi-classical expression for G can be found if one knows the classical trajectories starting at the point $\mathbf{r}$ and passing into the neighborhood of the point $\mathbf{r}$. Then $G = Ae^{iS}$, where S is determined by the Eq. (11). The meaning of A can be found if one makes use of Eq. (10). The surface of integration must be chosen so that it forms the boundary of a bundle of trajectories passing within a vanishingly small solid angle from point $\mathbf{r}$ and arriving in the neighborhood of the point $\mathbf{r}'$. Along such a surface $\partial S/\partial n$ reduces to zero, since $\partial S/\partial n$ is the component of the momentum normal to the trajectory. From this we find that $A^2(\mathbf{r}, \mathbf{r}')k(\mathbf{r}')df(\mathbf{r}')$ does not depend on $\mathbf{r}'$ (df is the transverse cross-section of the bundle of trajectories), and consequently, as $\mathbf{r} \to \mathbf{r}'$ (the length of the trajectory tends to zero) A^2 behaves like $a/|\mathbf{r} - \mathbf{r}'|^2$. The constant a must be chosen equal to unity, so that, as $\mathbf{r} \to \mathbf{r}'$,

$$G \to e^{ik|\mathbf{r}-\mathbf{r}'|}/|\mathbf{r} - \mathbf{r}'|.$$

With this normalization, $A = \sqrt{[k(\mathbf{r})/k(\mathbf{r}')]\, d\omega/df(\mathbf{r})}$ ($d\omega$ is the element of solid angle of the bundle of trajectories at the point $\mathbf{r}$).

If there are two or more trajectories connecting the points $\mathbf{r}$ and $\mathbf{r}'$, then, as follows from the principle of superposition, the Green's function is equal to

$$G = \sum A_\lambda e^{iS_\lambda}; \quad A_\lambda = \sqrt{[k(\mathbf{r})/k(\mathbf{r}')](d\omega/df)} \quad (12)$$

where the index λ designates the number of the trajectory.

2. Let us now go over to the finding of the semi-classical wave-functions for the scattering problem; these have the asymptotic form $e^{i\mathbf{k}_0\mathbf{r}} + \frac{F}{r} e^{ik_0 r}$. In order to find such wave functions in the semi-classical approximation, it is necessary to know the classical trajectories coming from infinity in the direction of the vector $\mathbf{k}_0$. The corresponding wave functions have the form $\psi_{\mathbf{k}_0} = \sum A'_\lambda e^{iS_\lambda}$, where the sum is taken over the various trajectories leading to the given point from infinity.

Let us examine the asymptotic behavior $\psi_{\mathbf{k}_0}(\mathbf{r})$.

As $\mathbf{r} \to \infty$ along a certain direction characterized by the unit vector $\mathbf{n}$, A'_λ falls off as $1/r$. An exception to this is the one term ($\lambda = \lambda_0$) corresponding to particles far from the scattering center, for which the cross-section of the tube of trajectories and the magnitude of the momentum are constant (Fig. 2). In this case we have $A'_{\lambda_0} = 1$ for the indicated normalization of $\psi_{\mathbf{k}_0}$. In agreement with Eq. (10), for the remaining λ, $A'_\lambda = \sqrt{df_0/df_\lambda}$ as $\mathbf{r} \to \infty$, where df_0 is the cross-section of the bundle of trajectories as $\mathbf{k}_0\mathbf{r} \to -\infty$ and $df_\lambda = r^2 d\Omega$, with $d\Omega$ the solid angle of the scattered bundle. It is obvious that $df_0/d\Omega = \sigma_\lambda$ is the classical differential cross-section. Thus, for $\lambda \neq \lambda_0$, A'_λ is given by $A'_\lambda = (1/r)\sqrt{\sigma_\lambda}$. The wave function, as $\mathbf{r} \to \infty$, consists of the sum of two terms: a plane wave (trajectory λ_0) and a diverging wave:

$$\psi \to e^{i\mathbf{k}_0\mathbf{r}} + \sum_{\lambda \neq \lambda_0} A'_\lambda e^{iS_\lambda} = e^{i\mathbf{k}_0\mathbf{r}} + \frac{e^{ikr}}{r}\sum_\lambda \sqrt{\sigma_\lambda}\, e^{i\varphi_\lambda}, \tag{13}$$

where σ_λ is the classical differential cross section calculated for a trajectory of type λ, while ϕ_λ, as follows from Eq. (11), is given by

$$\varphi_\lambda = \int k\, dl_\lambda - k_0 \int dl^* + \nu_\lambda \frac{\pi}{2} \tag{14}$$

The second integral is taken along two rays: from $-\infty$ along $\mathbf{k}_0$ to the origin, and from the origin to ∞ along $\mathbf{n}$; the infinities in each of the integrals mutually cancel each other. The integral $k_0 \int dl^*$ along the ray parallel to $\mathbf{n}$ arose from separating out the multiplier e^{ikr}, while on the other hand the integration along $\mathbf{k}_0$ originated in the multiplication of the ψ-function by that multiplying factor which reduces the phase of the plane wave to zero at $r = 0$. The last term of Eq. (14) is determined by the following circumstance: in the three-dimensional problem the semi-classical approximation turns out to be inapplicable near those points of the bundle of trajectories where the cross-sectional area of the bundle vanishes $(A \to \infty)$‡.

One can become convinced that in crossing such a point there appears an additional phase shift equal to $\pi/2$. In Eq. (14) ν_λ is the number of such points on the trajectory of type λ.

According to Eq. (13) the scattering cross section reduces to zero for scattering angles which are not attained in the classical mechanical solution. The scattering amplitude for these angles can be found by a method analogous to that used in the problem of the reflection from a barrier.

3. We shall seek a wave function in the form

$$\psi = \psi_0 + \psi_1,$$

where $\psi_0 = \sum_\lambda A'_\lambda e^{iS_\lambda}$. For ψ_1 we obtain

$$\Delta\psi_1 + k^2(\mathbf{r})\psi_1 = -\sum_\lambda \Delta A_\lambda' e^{iS_\lambda}.$$

If a Green's function satisfying the radiative condition is known, then the solution of the wave equation is

$$\psi = \psi_0 + \frac{1}{4\pi}\int G(\mathbf{r}'\mathbf{r}) \sum_\lambda \Delta A'_\lambda(\mathbf{r}')\, e^{iS_\lambda(\mathbf{r}')}\, d\mathbf{r}'. \tag{15}$$

The expression for the wave function can also be obtained in another way. Let us seek a wave function of the form

$$\psi = e^{i\mathbf{k}_0\mathbf{r}} + \psi_1.$$

Then for ψ_1 we obtain the equation

$$\Delta\psi_1 + k^2(\mathbf{r})\psi_1 = 2\, V e^{i\mathbf{k}_0\mathbf{r}};$$

by use of the Green's function we obtain a wave function having the required asymptotic form

$$\psi = e^{i\mathbf{k}_0\mathbf{r}} - \frac{1}{2\pi}\int G(\mathbf{r}'\mathbf{r})\, V(\mathbf{r}')\, e^{i\mathbf{k}_0\mathbf{r}'}\, d\mathbf{r}'. \tag{16}$$

For the Green's function it is sufficient to apply the semi-classical expression (12). Choosing as an initial expression not ψ_0 but ψ, one can obtain the following approximation with respect to the parameter ξ.

4. Let us examine in more detail the case in which the potential is small compared with the energy of the particle ($|V| \ll E = k^2/2$). This condition, as is well known, does not indicate the application of the perturbation theory. As a criterion for the applicability of the perturbation theory, we have the requirement:

$$\frac{|V|}{E}\frac{l}{\lambda} \ll 1,$$

‡For this remark I am indebted to V. S. Kudryavtsev.

where l is a length characterizing the variation of the potential, and $\lambda\!\!\!^{-}$ is the wave-length of the particle.

In the case $V \ll E$ the trajectories are nearly rectilinear , and the computation is considerably simplified. It is easy to show that in order to obtain the terms linear with respect to the potential in the function S one need carry out the integration only along rectillinear trajectories. Indeed, let K_0 be the momentum of the particle moving in a potential V_0, dl_0 an element of length of the trajectory. The change in S upon changing the potential by the amount δV will be

$$\delta S = \int \delta k dl_0 + \int k_0 \delta dl.$$

The second term consists of the change in S due to variation of the trajectory with the potential left unchanged. On account of the stationary character of S this term is quadratic in δl,and consequently, in δV. Therefore, to within terms of second order in δV,

$$\delta S = \int \frac{\delta V}{k_0} dl_0.$$

In this way δS is determined by an integral along the unperturbed trajectory.

Since in the case under study there is only one rectilinear trajectory connecting the points $\mathbf{r}$ and $\mathbf{r}'$ for the unperturbed problem (free motion), the Green's function takes the form

$$G = \frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \exp\left\{i\int_{\mathbf{r}'}^{\mathbf{r}} (k-k_0)\, dl\right\}. \quad (17)$$

The integration is carried out along a straight line connecting points $\mathbf{r}'$ and $\mathbf{r}$.

With the use of the Green's function (17) we find from Eq. (16)

$$\psi = e^{i\mathbf{k}_0\mathbf{r}} - \frac{1}{2\pi}\int \frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad (18)$$

$$\times\ V(\mathbf{r}') \exp\left\{i\mathbf{k}_0\mathbf{r}' - \frac{i}{k_0}\int_{\mathbf{r}}^{\mathbf{r}'} V\, dl_1\right\} d\mathbf{r}',$$

where dl_1 is an element of the rectilinear trajectory connecting points $\mathbf{r}'$ and $\mathbf{r}$. The wave function can be written in the form

$$\psi = e^{i\mathbf{k}_0\mathbf{r}}\left(1 - \frac{1}{2\pi}\int \frac{e^{ik_0\rho}}{\rho} V(\mathbf{r}+\vec{\rho})\right.$$

$$\left.\times\ \exp\left\{i\mathbf{k}_0\vec{\rho} - \frac{i}{k_0}\int_0^{\rho} V\left(\mathbf{r} + l_1\frac{\vec{\rho}}{\rho}\right) dl_1\right\} d\vec{\rho}\right).$$

Here the vector $\vec{\rho} = \mathbf{r}' - \mathbf{r}$.

Let us carry out the integration over the angles of the vector $\vec{\rho}$, using the fact that in varying the angle between $\vec{\rho}$ and $\mathbf{k}_0$, the factor $e^{i\mathbf{k}_0\vec{\rho}}$ oscillates extremely rapidly. Integrating by parts and keeping the first term of order $\xi = 1/k_0 l$, we obtain

$$\psi = e^{i\mathbf{k}_0\mathbf{r}}\left(1 + \frac{i}{k_0}\int_0^{\infty} \exp\left\{ik_0\rho - \frac{i}{k_0}\int V dl_1\right\}\right.$$

$$\times\left\{V\left(\mathbf{r} + \rho\frac{\mathbf{k}_0}{k_0}\right)e^{ik_0\rho}\right.$$

$$\left.\left. - V\left(\mathbf{r} - \rho\frac{\mathbf{k}_0}{k_0}\right)e^{-ik_0\rho}\right\} d\rho\right).$$

Within a precision of the order of the quantity ξ it is permissible to discard the term under the integral sign containing the rapidly oscillating factor $e^{2ik_0\rho}$. Therefore we obtain

$$\psi = e^{i\mathbf{k}_0\mathbf{r}}\left(1 - \frac{i}{k_0}\int_0^{\infty} d\rho V\left(\mathbf{r} - \rho\frac{\mathbf{k}_0}{k_0}\right)\right.$$

$$\left.\times\ \exp\left\{-\frac{i}{k_0}\int_0^{\rho} V\left(\mathbf{r} - \rho_1\frac{\mathbf{k}_0}{k_0}\right) d\rho_1\right\}\right)$$

$$= e^{i\mathbf{k}_0\mathbf{r}} \quad (19)$$

$$\times\left(1 - 1 + \exp\left\{-\frac{i}{k_0}\int_0^{\infty} V\left(\mathbf{r} - \rho_1\frac{\mathbf{k}_0}{k_0}\right) d\rho_1\right\}\right)$$

$$= \exp\left\{i\mathbf{k}_0\mathbf{r} - \frac{i}{k_0}\int_{-\infty}^{h} V\, dl_0\right\}.$$

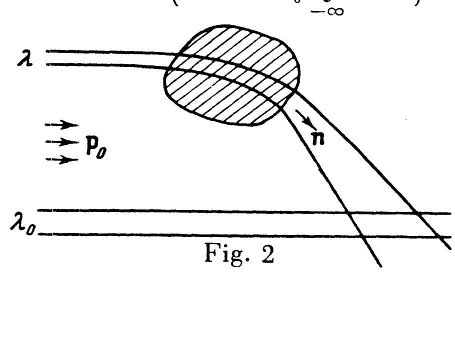

Fig. 2

Equation (19) is the well-known expression for the semi-classical wave function at finite distances from the scattering center[1].

Let us find the asymptotic form of the wave function as $r \to \infty$. From Eq. (19) we find

$$\psi = e^{i\mathbf{k}_0\mathbf{r}}$$

$$-\frac{e^{ik_0 r}}{r}\left[\frac{1}{2\pi}\int \exp\left\{i\mathbf{q}\mathbf{r}' + \frac{i}{k_0}\int_{\mathbf{r}'}^{\infty} V dl_1\right\} V(\mathbf{r}')\, d\mathbf{r}'\right]$$

$$(\mathbf{q} = \mathbf{k}_0 - k_0\mathbf{n}),$$

where $\mathbf{n}$ is a unit vector in the direction $\mathbf{r}$, dl_1 is an element of the rectilinear trajectory parallel to $\mathbf{n}$. The integral in the exponent of the exponential function can be also written in the form

$$\int_{\mathbf{r}'}^{\infty} V dl_1 = \int_0^{\infty} V(\mathbf{r}' + r_1\mathbf{n})\, dr_1.$$

Thus the scattering amplitude is given by the expression

$$f = -\frac{1}{2\pi}\int \exp\left\{i\mathbf{q}\mathbf{r}' + \frac{i}{k_0}\int_0^{\infty} V(\mathbf{r}' + r_1\mathbf{n})\, dr_1\right\} V(\mathbf{r}')\, d\mathbf{r}', \tag{20}$$

which reduces to the result of perturbation theory for sufficiently small V.

The scattering at large angles, for $V \ll E$, which is not contained in the classical solution of the problem, can be found from Eq. (20). For this we introduce integration by parts with respect to the cosine of the angle between the vectors $\mathbf{r}'$ and $\mathbf{q}$, considering that the expression $e^{i\mathbf{q}\mathbf{r}}$ oscillates rapidly, and we shall keep only the term of the series of order $\xi = 1/k_0 l$:

$$f = -\int \exp\left\{iqr'x + \frac{i}{k_0}\int_{r_1}^{\infty} V dl_1\right\} V(\mathbf{r}')\, dx\, r'^2 dr'$$

$$\approx -\int_0^{\infty} \frac{r'^2 dr'}{iqr'}\left[V\left(r'\frac{\mathbf{q}}{q}\right) e^{iqr'} \exp\left\{\frac{i}{k_0}\int_0^{\infty} V\left(r\frac{\mathbf{q}}{q} + r_1\mathbf{n}\right) dr_1\right\} - V\left(-r' - \frac{\mathbf{q}}{q}\right) e^{-iqr'} \exp\left\{\frac{i}{k_0}\int_0^{\infty} V\left(-r\frac{\mathbf{q}}{q} + r_1 n\right) dr_1\right\}\right].$$

Two terms of the square bracket can be combined, so that

$$f = \frac{i}{q}\int_{-\infty}^{+\infty} r'dr' V\left(r'\frac{\mathbf{q}}{q}\right) \exp\left\{iqr' + \frac{i}{k_0}\int_0^{\infty} V\left(r'\frac{\mathbf{q}}{q} + r_1\mathbf{n}\right) dr_1\right\}. \tag{21}$$

Equation (21) recalls the formula for the reflection coefficient in the one-dimensional problem, and it is extremely convenient for integration in the complex plane.

[1] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, part I, p. 184, 1948

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