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Finite total three-particle scattering rates*

Roger G. Newton and Roman Shtokhamer†
Physics Department, Indiana University, Bloomington, Indiana 47401
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It is shown that, despite the double-scattering infinities of the differential scattering rates for three particles, the total scattering rates for three particles are unambiguous and finite. These rates are expressed in terms of T-matrix elements by means of a well-defined principal value of an integral whose integrand has a double pole. We also derive an expression for the double-scattering rate.

I. INTRODUCTION

It is now well understood[1–5] that the differential scattering rate of three colliding particles tends to infinity as those final momenta of the particles are approached at which real, energy-conserving double scattering is possible. What is more, the scattering amplitude grows at a rate that makes it fail to be square integrable. As a result, the calculation of a total scattering rate, and of inclusive rates, for three incident particles, when based on the known expressions for the amplitude, always yield the physically unpallatable answer, infinity.

In the present paper we show that if the total or inclusive rates are calculated in a manner that differs somewhat from a straightforward integration of the previously known differential rate but which is physically meaningful and mathematically unambiguous, they are *finite*. We arrive at this conclusion from a time-independent point of view and we discuss the physical meaning of the various terms we obtain in the answer. The dominant contribution of the result so derived originates from the double scattering, but the method makes it difficult to interpret this unambiguously in terms of a scattering rate. We therefore separately employ the time-dependent method of scattering theory, that is, normalizable states or wave packets, to derive a double-scattering rate that depends in a simple and physically meaningful way on the experimental arrangement. We also briefly discuss the implication of our results for the calculation of the third virial coefficient of gases and for that of chemical reaction rates.

There are five appendixes: Appendix A defines the Jacobi coordinates of three particles in their center-of-mass system. Appendix B contains the details of the stationary-phase evaluation of the asymptotic wave function. Appendix C give details of the integration of the squared modulus of the wave function. Appendix D defines the principal value of an integral containing a double pole in its integrand, and Appendix E deals with the impact parameters needed for the wave-packet description.

II. QUALITATIVE SUMMARY

In Secs. III and IV we work in a time-independent framework, in the center-of-mass system. Jacobi coordinates will be used as in Ref. 4. They are explicitly defined in Appendix A. We write

$$G_0^+(E) = (E + i\epsilon - H_0)^{-1}, \tag{2.1}$$

$$V_i = V_i(\vec{r}_i), \quad i = 1,2,3, \tag{2.2}$$

$$G_i^+(E) = (E + i\epsilon - H_0 - V_i)^{-1} = G_i^{+C} + G_i^{+B}, \tag{2.3}$$

where G_i^{+C} and G_i^{+B} are the continuum and the bound-state parts of G_i^+, as defined explicitly in Eqs. (2.10) and (2.11) of Ref. 4.

The time-independent wave function of three particles, all three being incident freely, can be decomposed as follows[4]:

$$\psi^{(+)} = \psi_0 + \psi_1 + \psi_2 + \psi_3 + \psi_4, \tag{2.4}$$

where

$$\begin{aligned}
&\psi_0 = e^{i\vec{K}\cdot\vec{R}}, \quad \psi_1 = \sum_i G_i^+ V_i \psi_0, \\
&\psi_2 = \sum_{i\neq j} G_i^{+B} V_i G_0^+ V_j \psi^{(+)}, \\
&\psi_3 = \sum_{i\neq j} G_i^{+C} V_i G_0^+ V_j \psi_j^{(+)}, \\
&\psi_4 = \sum_{i\neq j} G_i^{+C} V_i G_0^+ V_j G_j^+ \sum_{l\neq j} V_l \psi^{(+)},
\end{aligned} \tag{2.5}$$

and

$$\psi_j^{(+)} = \psi_0 + G_j^+ V_j \psi_0. \tag{2.6}$$

The function ψ_0, of course, describes the three incident free particles; ψ_1 describes single scattering, and ψ_2 describes the formation of bound pairs in the outgoing wave. We are not interested in any of these parts of the wave function in this paper. The function ψ_4 tends to zero at large distances as $O(R^{-5/2})$, and it describes, in an unambiguous way, a part of the "true" three-particle scattering. It causes no difficulties, and we shall be interested in it only in so far as it eventually contributes a part of the scattering rate. We shall return to it at the appropriate time.

The part of the three-particle wave function that causes the double-scattering difficulties is

$$\psi_3 = \sum_{i \neq j} \psi^{(ij)} , \tag{2.7}$$

$$\psi^{(ij)} = G_i^{+C} V_i G_0^+ V_j \psi_j^{(+)} , \tag{2.8}$$

and our attention will focus principally on it. Let us remind ourselves[4] of the large-distance behavior of $\psi^{(ij)}$.

As $R \to \infty$ the function $\psi^{(ij)}$ contains as its leading contributions two terms, one that goes as R^{-2}, and another as $R^{-5/2}$, with a remainder $o(R^{-5/2})$. The R^{-2} term is identified as having the physical significance of describing the double scattering in which the pair j (that is, particles i and l, $j \neq l \neq i$) collides first on the energy shell, followed by the collision of the pair i.[6] For given initial momenta, such a double collision is energetically possible only at certain specific final momenta, which are determined by the conservation equations[7]

$$q_j = q_j'' , \quad \vec{k}_j = \vec{k}_j'' , \quad q_i' = q_i'' , \quad \vec{k}_i' = \vec{k}_i'' , \tag{2.9}$$

using unprimed letters for the initial momenta, primed letters for the final ones, and double-primed letters for the intermediate momenta, after the first collision. Final momenta are identified in the wave function as distance ratios and directions. (Exactly how this happens mathematically was shown in Ref. 4, and we shall see it again below.) Physically this is because if particles collide at the origin, they will then be found later at points whose directions from the origin correspond to their momentum directions and whose distance ratios correspond to their velocity ratios.[8] The total energy being given, specification of the final momenta therefore corresponds to specification of the direction of $\vec{R}$ in six-dimensional space.

If we fix the direction of the six-dimensional vector $\vec{R}$ at a value that corresponds to momenta for which double scattering is energetically possible, then the leading term in ψ_3 goes as R^{-2} and the factor of R^{-2} determines the double-scattering rate. We shall refer to this direction in 6-space as the double-scattering *ridge*, or simply the ridge. On the ridge, then, the asymptotic behavior of $\psi^{(ij)}$ as $R \to \infty$ is a constant multiple of $R^{-2} e^{iK_{ij}R}$, where $\vec{K}_{ij}$ is determined by the double-scattering equations (2.9).

In the other directions of 6-space, away from the ridge, the leading term of $\psi^{(ij)}$ is also $O(R^{-2})$, but as $R^{-2} e^{i\vec{K}_{ij}\cdot\vec{R}}$. Since $\vec{R}$ is not along the ridge now, its direction is not parallel to $\vec{K}_{ij}$ and hence the wave is not spherical. This term describes the propagation of double-scattered particles not coming from the center. The physical reason for this is easy enough to understand: Double scattering can take place with large distances between the two collisions and hence the particles from the second collision, seen at a given point, need not come from the center. This fact imparts to the double collisions, in effect, a very long range, and it may be regarded as the physical origin of the double-scattering problems, which in some ways are analogous to those arising in the forward direction for long-range potentials.

The next-to-leading term in $\psi^{(ij)}$ off the ridge, as $R \to \infty$, goes as $R^{-5/2} e^{iKR}$, and its factor forms one of the contributions to the "true" three-three scattering. (The others come from ψ_4.) It may be thought of as an off-energy-shell contribution of the double scattering. Its most important characteristic is the fact that as the ridge is approached it tends to infinity in a manner that is not square integrable. The "true" differential 3-3 scattering rate, which is in principle well observable,[9] and which is theoretically described by the squared magnitude of the factor of $R^{-5/2}$ in $\psi_3 + \psi_4$, consequently tends to infinity as the double-scattering momenta are approached. Furthermore, any attempt to calculate the total "true" 3-3 rate, or an inclusive one, leads to an infinite result. Indeed, because this is so, even the calculation of the total 3-3 rate, including all of the observed particles, whether double-scattered or not, cannot be regarded as satisfactory even if the double-scattering rate is finite, so long as the "true" 3-3 rate comes out infinite. The solution of this problem is therefore necessary for the reliability of all calculated total 3-3 rates.

Mathematically the problem arises from a nonuniform behavior of the function $\psi^{(ij)}$ in its dependence on the magnitude and the direction of $\vec{R}$. The "true" 3-3 amplitude is defined by fixing the direction of $\vec{R}$ at a generic value and picking out the factor of $R^{-5/2}$ as $R \to \infty$. As we then allow[7] $\hat{R}$ to approach the ridge, this factor tends to infinity. If, on the other hand, we let $\hat{R}$ approach the ridge first, then $\psi^{(ij)}$ remains finite, even in the limit as $R \to \infty$. The two limits are not interchangeable.

As we shall show, the solution to the difficulty is to examine the behavior of $\psi^{(ij)}$ *near* the ridge, as was done by Nuttall[2] and Merkuriev,[3] who found it well described in terms of a Fresnel function. If this description is used,[11] the squared magnitude of ψ is integrated over a region that includes the ridge, and R is allowed to grow to infinity only after the integration, then one obtains a finite result whose two leading terms go as R^{-4} and R^{-5}. We shall derive these terms and interpret them physically in Sec. IV.

We shall see, however, that this procedure does not lend itself easily to the derivation of a double-scattering rate in given experimental circumstances. We therefore approach the problem in Sec. V from a wave-packet point of view and derive there a rate for double scattering that depends in a simple and physically meaningful way on the experimental arrangement.

III. ASYMPTOTIC FORM OF THE WAVE FUNCTION

It was shown in Ref. 4 that $\psi^{(ij)}$ can be written as follows[13]:

$$\psi^{(ij)}(\vec{R}) = [2(m_1m_2m_3)^{1/2}/i\pi M^{1/2}r_i\rho_i]\xi_{ij} , \qquad (3.1)$$

where for large R

$$\frac{1}{\rho_i}\xi_{ij} = \frac{i}{2\pi}\int d^3k_i''\exp[i\vec{k}_i\cdot\vec{\rho}_i + i(E-k_i''^2)^{1/2}r_i] \times\frac{h_{ij}}{b_{ij}^2(q_j''^2-q_j^2-i\epsilon)} + o(R^{-3/2}) , \qquad (3.2)$$

$$h_{ij} = A_i^{(-)}((E-k_i''^2)^{1/2}\hat{r}_i, \vec{q}_i'')A_j^{(+)}(\vec{q}_j'', \vec{q}_j) . \qquad (3.3)$$

The unprimed momentum components are the initial momenta, and $\vec{q}_i''$ and $\vec{q}_j''$ are defined by[14]

$$-b_{ji}\vec{q}_i'' = \vec{k}_j - a_{ji}\vec{k}_i'' , \quad -b_{ij}\vec{q}_j'' = \vec{k}_i'' - a_{ij}\vec{k}_j , \qquad (3.4)$$

a_{ij} and b_{ij} being defined by (A3). The function $A_j^{(+)}$ is the off-shell scattering amplitude of the pair j,

$$A_j^{(+)}(\vec{q}', \vec{q}) = -\frac{1}{4\pi(2\mu_j)^{1/2}}\int d^3r\, e^{-i\vec{q}'\cdot\vec{r}}\,V_j(\vec{r})\psi_j^{(+)}(\vec{q}, \vec{r}) , \qquad (3.5)$$

and $A_i^{(-)}$ is the other off-shell amplitude,

$$A_i^{(-)}(\vec{q}', \vec{q}) = -\frac{1}{4\pi(2\mu_i)^{1/2}}\int d^3r\,\psi_i^{(-)*}(\vec{q}', \vec{r})V_i(\vec{r})e^{i\vec{q}\cdot\vec{r}} . \qquad (3.6)$$

We are interested in the asymptotic value of ξ_{ij} as r_i and ρ_i both tend to infinity with the fixed ratio

$$\gamma = \rho_i/r_i . \qquad (3.7)$$

This asymptotic value is obtained from (3.2) by the method of stationary phase, applied three times, in each of the three integrations of (3.2). In contrast to Ref. 4 we shift variables and use $\vec{q}_j''$, defined by the second equation in (3.4), as the integration variable. The two angle integrations are straightforward, but the integration over q_j'' is complicated by the zero in the denominator of (3.2). This is what, mathematically, gives rise to the double-scattering problem.

We relegate the details of the evaluation of the integrals to Appendix B. The result is

$$\psi^{(ij)} = R^{-5/2}e^{iKR}\xi_{ij} + o(R^{-5/2}) ,$$

where ξ_{ij} has three different forms, depending on whether $\vec{R}$ is on the double-scattering ridge, near it, or away from it[15]: On the ridge,

$$\xi_{ij} = R^{1/2}\delta(\tfrac{1}{2}\pi)^{1/2}e^{-i\pi/4}h_{ij} + O(1) ; \qquad (3.8a)$$

near the ridge,

$$\xi_{ij} = R^{1/2}\delta\left((2\pi)^{1/2}h_{ij}e^{i\pi/4-ia^2x^2/2}\theta(x) - \frac{i}{a}\frac{\partial h_{ij}}{\partial q_j''} - h_{ij}\,\mathrm{sgn}x\,F(a|x|)\right) ; \qquad (3.8b)$$

and off the ridge,

$$\xi_{ij} = 2R^{1/2}\delta e^{-i\pi/4}h_{ij}(\tfrac{1}{2}\pi)^{1/2} \times\exp[i(r_iq_i^d + \vec{\rho}_i\cdot\vec{k}_i^d) - iKR]\theta(x) + \frac{2^{3/2}K^{3/2}e^{i\pi/4}h_{ij}(q_{js})(m_1m_2m_3)^{1/2}}{\pi^{1/2}M^{1/2}|b_{ij}|^2(q_j^2-q_{js}^2)} , \qquad (3.8c)$$

with

$$\delta = \frac{\nu K(1+\gamma^2)^{1/2}(m_1m_2m_3)^{1/2}}{(\frac{1}{2}\pi)^{1/2}|b_{ij}|M^{1/2}q_j}e^{i\pi/4} , \qquad (3.9)$$

and with q_{js} being the value of q_j'' where the phase is stationary. In the "near-ridge" value all functions except x are evaluated at $q_j'' = q_{js}$. The remaining symbols are defined in (B11), and $F(x)$ is the Fresnel function defined in (B12). The ridge is located at $x=0$, and the limiting values of F, given by (B13) and (B14), make the near-ridge value of ξ_{ij} in (3.8) go over into the on-ridge value for $x=0$, and also fit continuously to the off-ridge values in the following sense: If we keep $x\neq 0$ fixed in the near-ridge value and allow R to become large, then its asymptotic value is the off-ridge function for small x, plus $o(1)$. It follows from the second equation of (3.4) and Eq. (A6) that the stationary $\vec{q}_{js}$ corresponds to $\vec{k}_{is}$ being parallel (or antiparallel) to $\vec{\rho}_i$. This is what we call the final momentum:

$$\vec{k}_i' = k_{is}\hat{\rho}_i . \qquad (3.10)$$

In view of (3.3) we also call

$$\vec{q}_i' = (E-k_i''^2)^{1/2}\hat{r}_i \qquad (3.10')$$

the other final momentum. Similarly,

$$\vec{q}_j' = \vec{q}_{js} . \qquad (3.10'')$$

According to Ref. 4, the asymptotic behavior of $\psi_3 + \psi_4$ is now given by

$$\psi_3 + \psi_4 = R^{-5/2}e^{iKR}\left(\sum_{i\neq j}\xi_{ij} + A_{00}^T\right) + o(R^{-5/2}) , \qquad (3.11)$$

where A_{00}^T comes from ψ_4 and is given explicitly by (4.33) of Ref. 4. It is continuous in all directions. The double-scattering difficulty, on the other hand, is clearly visible in the off-ridge value of ξ_{ij} in

(3.8). This is the off-shell contribution of the double scattering, and together with A_{00}^T its squared magnitude describes the "true" differential 3-3 scattering rate. As $q_{js}^2 \to q_j^2$, i.e., as we approach on-shell double scattering, it diverges. However, if we do not take the asymptotic value but keep R finite and retain the form (3.8b) near the ridge, then ψ remains continuous. We shall exploit this fact to evaluate the flux at finite R, and only subsequently allow R to increase to infinity.

IV. INTEGRATION

We will want to integrate[16] $|\psi|^2$ over a spherical surface of radius R in the six-dimensional $\vec{R}$ space, where

$$d^6\vec{R} = R^5\, dR\, d\hat{R} = d^3\vec{\rho}_i\, d^3\vec{r}_i = d\hat{\rho}_i\, d\hat{r}_i\, \rho_i^2 r_i^2\, d\rho_i\, dr_i\,.$$

Using the variables R and γ as given by (A7) and (3.7), we have

$$\frac{\partial(R,\gamma)}{\partial(\rho_i, r_i)} = \frac{R}{r_i^2}\,,$$

so that

$$d\rho_i\, dr_i = r_i^2 R^{-1}\, dR\, d\gamma\,,$$

and hence the surface element in six dimensions is

$$R^5\, d\hat{R} = d\hat{r}_i\, d\hat{\rho}_i\, d\gamma\, \gamma^2(1+\gamma^2)^{-3} R^5\,. \qquad (4.1)$$

For the calculation of a total scattering rate we have to integrate $|\psi|^2$ over all directions of $\hat{R}$ or over all three-dimensional solid angles of $\hat{\rho}_i$ and $\hat{r}_i$, and over γ from 0 to ∞, in any order.[17] We choose to integrate first over the direction of $\hat{\rho}_i$. Since θ is the angle between $\vec{\rho}_i$ and $\vec{k}_j$, this means integrating with $d\theta \sin\theta$ from 0 to π. The integration over the azimuthal angle φ_i will be kept in abeyance.

For a given value of γ, the angle θ_s may be eliminated from (B2) and (B4), or from (B6) and (B8′). Setting

$$\alpha = \gamma/(1+\gamma^2)^{1/2}\,,$$

we obtain

$$b_{ij}^2 q_{js}^2 = a_{ij}^2 k_j^2 + \alpha^2 E - 2\alpha K a_{ij} k_j \cos\theta\,, \qquad (4.2)$$

which shows that in the domain $0 \le \theta \le \pi$, q_{js} is a monotonic function of θ, with the range[18]

$$\frac{|a_{ij}k_j - \alpha K|}{|b_{ij}|} \le q_{js} \le \frac{|a_{ij}k_j + \alpha K|}{|b_{ij}|}\,. \qquad (4.3)$$

We may therefore change variables of integration and use q_{js} in place of θ, with

$$d\theta \sin\theta = [b_{ij}^2(1+\gamma^2)^{1/2}/\gamma K a_{ij} k_j]\, q_{js}\, dq_{js}\,. \qquad (4.4)$$

Note that because of the appearance of γ^2 in (4.1), the γ in the denominator of (4.4) causes no problem. We have

$$d\hat{R} = (b_{ij}^2/K|a_{ij}|k_j)\, d\gamma\, \gamma(1+\gamma^2)^{-5/2}\, d\hat{r}_i\, d\varphi_i\, dq_{js}\, q_{js}\,. \qquad (4.5)$$

The q_{js} integration is going to be performed by doing separately the integral over the vicinity of the ridge, $q_{js} = q_j$, and the remaining integrals. We then have near the ridge

$$\int_{q_j-\epsilon}^{q_j+\epsilon} dq_{js} \cdots = \int_{-\epsilon}^{\epsilon} dx\,,$$

where $\epsilon \ll 1$. In these integrals we use the near-ridge value given in (3.8b).

To be specific, for the purpose of ordering terms, we shall assume that

$$K^{-3}\epsilon^4 R \ll 1\,. \qquad (4.6)$$

In the other two integrals we want to use the off-ridge value given in (3.8c). Since the latter is obtained by allowing xa to become large, we must assume that

$$K^{-1/2}\epsilon R^{1/2} \gg 1\,. \qquad (4.7)$$

In fact, it will be convenient to make the stronger assumption

$$K^{-2}\epsilon^3 R \gg 1\,. \qquad (4.8)$$

Our approach will be as follows: In the off-ridge region we keep only the $R^{-5/2}$ terms of (3.8c), together with the $R^{-5/2}$ terms in the remainder of $\psi_3 + \psi_4$. In this region the R^{-2} terms are physically distinguishable from the $R^{-5/2}$ terms, and as discussed earlier they represent the doubly scattered particles that come from directions other than the center, because their second collision took place far from it. They are distinguishable from the "truly" 3-3 scattered particles by their momentum. However, the more closely the counters approach the ridge, the harder it is to distinguish doubly scattered particles from the others. Therefore in the region near the ridge we must keep both. This is analogous to the situation in the forward scattering of a particle by a center, where scattered particles near the forward directions become less and less distinguishable from unscattered ones.[19]

We perform the details of these calculations in Appendix C. The result of adding the two contributions, near the ridge and off the ridge, is given by (C17) and (4.5) to be of the form

$$R^4 \int d\hat{R}\,|\psi_3+\psi_4|^2 = \frac{b_{ij}^2}{K|a_{ij}|k_j} \int d\gamma \frac{\gamma}{(1+\gamma^2)^{5/2}} d\hat{r}_i\, d\varphi_i \left[2\pi q_j^3 |\delta|^2 |h_{ij}|^2 \epsilon + R^{-1} \mathcal{P} \int dq_{js} \left| \frac{C_5}{q_j^2 - q_{js}^2} + C_6 \right|^2 + 2\pi q_j^3 |\delta|^2 c^{-2}\,\mathrm{Im}\left(h_{ij}^* \frac{\partial h_{ij}}{\partial q_j''} \right) R^{-1} + 2\pi q_j^3 |\delta|^2 c^{-1}\,\mathrm{Re}(h_{ij}^* c_4) R^{-1} \right] + o(R^{-1})\,. \qquad (4.9)$$

Let us look at this result in some detail.

The first notable point is that it is finite and contains only terms of order 1 and of order R^{-1}. To be specific, there are no terms of order $R^{-1/2}$. It is shown explicitly in Appendix C that the $R^{-1/2}$ terms cancel.

The leading term on the right-hand side of (4.9) is the first, because of (4.7). This term, of course, describes the double scattering. It counts only the doubly scattered particles that come from the center. For most physical applications these are the only ones of interest. However, because of the dependence of this term on ϵ, which in a sense is a measure of the width of the ridge, it is difficult to interpret it directly as a collision rate. In order to obtain such a rate in terms of physical parameters we are going to derive an expression for it in Sec. V from a wave-packet point of view.

The second term in (4.9) is the one that describes the total rate of "true" 3-3 scattering. The combination, the square of whose modulus appears in the integrand, is just the sum of terms that makes up what in Ref. 4 is called

$$A_{00} = A_{00}^D + A_{00}^T\,,$$

the "true" three-particle amplitude. It is simply obtained from the T matrix after subtracting the three 2-particle T matrices.[21] The significance of (4.9) is that it gives a prescription for the evaluation of the integral which in a straightforward manner of evaluation would diverge.

The "dangerous" part of the integral has a pole of *second* order. The prescription which renders the integral finite is called a principal value and defined in Appendix D. It is a reasonable extension of the definition of the well-known Cauchy principal value of an integral that contains a simple pole in its integrand. We show in Appendix D that if the residue is continuous then the principal-value integral there defined is finite. Appendix C shows explicitly how this particular evaluation of the integral is justified by the combination of terms that arise from (3.8). We emphasize that this evaluation is not arbitrary; the combination of terms that arise from the integrals near the ridge is exactly that given in (D3). We thus have not only a finite total "true" 3-3 scattering rate, but a simple method of evaluating it. In view of (4.37) of Ref. 4 we may write for the total "true" 3-3 rate

$$\sigma = \frac{\bar{\mu}_i k_i'}{2^{5/2} m_i^2 \mu_i^{3/2} K^3 k_i} \mathcal{P} \int d^3q_i'\, d\hat{p}_i'\, |A_{00}|^2\,. \qquad (4.10)$$

It is explicitly pointed out in Appendix D that the principal value there defined has the counterintuitive property of not necessarily being positive when the integrand "looks" positive definite. This means that we have no *a priori* guarantee that the integral in (4.10) is positive. This is, of course, disturbing, since a negative value would be incompatible with an interpretation as a number of particles, or of particle triples. We are inclined to interpret our result as an additional physical requirement: The three-particle T matrix must be such as to make the integral in (4.10) positive. If there are T matrices that fail to have this property, we do not know how to interpret (4.9) and (4.10) for them.

The physical significance of the remaining two terms in (4.9) is less clear. They are interference terms between the "true" 3-3- and the double scattering. Note that both are of order R^{-1} and independent of ϵ, i.e., free of arbitrariness. As the interferences in a double-slit diffraction experiment, they arise in a fundamental way from the indistinguishability of "true" 3-3 scattering from double scattering at and near the double-scattering momenta. In a sense that is, of course, understandable only quantum mechanically, they count the number of triples of particles that have been *both* double scattered and "truly" 3-3 scattered.

V. WAVE-PACKET APPROACH

We now consider the scattering of three wave packets by each other, as described in the general case in Ref. 10. The central idea is to calculate first the conditional probability P_b that the particles at some time cross a given surface, on the assumption that the incoming wave packet is centered at a given impact-parameter vector b^B; then we shall calculate the probability $\rho(b^B)\,db^B$ that the incoming packet is centered in the impact-parameter element db^B; and hence we shall conclude that for a thus incoherently distributed beam the probability is given by

$$P = \int db^B \rho(b^B) P_b\,. \qquad (5.1)$$

In the case of three particles the impact-parameter space is five dimensional. This is because displacing the center of mass or shifting all wave packets along their tracks in proportion to their velocities will not alter their relative positions at the time of collision. Hence four of their nine degrees of freedom are irrelevant. We explicitly introduce in Appendix E the split of the nine-dimensional configuration space into a five-dimensional impact-parameter space and its orthogonal complement. The components of a set of three vectors $\vec{x}_i$, $i=1,2,3$, in the latter are called x_i^F, $i=1,\ldots,4$, and in the former, x_i^B, $i=5,\ldots,9$. The metric is such that

$$\sum_{i=1}^{3} m_i \vec{x}_i^2 = \sum_{j=1}^{4} x_j^{F2} + \sum_{j=5}^{9} x_j^{B2} . \tag{5.2}$$

For "true" 3-3 scattering we have the following situation:

(i) In a given beam, the b_i^B are, of course, bounded. However, we make the assumption (a) that, as was explicitly discussed in Ref. 10, they must be allowed to become large enough that the decrease of P_b as a function of b^B permits us to extend the integral in (5.1) to infinity without appreciable error.[22] In fact, we must assume (b) that the (macroscopic) radii of the beams are very large compared to the maximal (microscopic) impact parameters that contribute to the scattering, i.e., to the integral in (5.1). These assumptions are important for the calculation of the density $\rho(b^B)$, which is determined by the requirement that [by (E11)]

$$\begin{aligned}\rho(b^B)\, d^5b^B &= \int d^3b_1\, d^3b_2\, d^3b_3 \prod_{i=1}^{3} \rho^{(i)} \\ &= \int d^4b^F \left(\prod_i \rho^{(i)}\right) d^5b^B \left(\prod_i m_i\right)^{-3/2},\end{aligned} \tag{5.3}$$

with

$$\int \rho(b^B)\, d^5b^B = 1 . \tag{5.4}$$

Here $\rho^{(i)}$ is the density of the ith beams, which we assume to be uniform over the length[23] $T_i \vec{v}_i^0 = T_i \vec{p}_i^0/m_i$ and the cross section πa^2. Thus T_i is the duration of the ith beam, and inside the volume

$$V_i = \pi a^2 v_i^0 T_i \tag{5.5}$$

the beam density has the constant value

$$\rho^{(i)0} = 1/V_i . \tag{5.6}$$

Assumption (b) allows us to set $b^B=0$ in the integration (5.3). It was shown in Ref. 10 that as a result[24]

$$\rho(b^B) = (2E^0)^{1/2} M^{3/2} \left(\prod_i \rho^{(i)}\right)\left(\prod_i m_i\right)^{-3/2} V_{\rm int} T . \tag{5.7}$$

Here T is the time during which all three beams fully intersect.

(ii) Another assumption that has been used in the derivation of (5.7) is that T is so large that the "edge effects" due to partial intersection of the beams are relatively negligible. The quantity $V_{\rm int}$ is the volume of the three-dimensional spatial region of intersection of the three beams.

The use of (5.7), together with the calculation of P_b as given in Ref. 10, leads to the rate at which "truly" 3-3 scattered particles will be found crossing a distant surface intersecting the cone C,

$$R = V_{\rm int} \left(\prod_i d_i\right) \sigma , \tag{5.8}$$

where $d_i = N_i/V_i$ is the particle density of the ith beam if N_i is the number of particles of kind i, and σ is the specific scattering rate[25]

$$\sigma = (2\pi)^7 \int_C d^9k' \,|\, T_{E_0}(k', k_0)|^2 \delta(E' - E_0)\, \delta^3(\vec{K} - \vec{K}_0) . \tag{5.9}$$

In the case of double scattering there will be a non-negligible number of events that come from large impact parameters b^B, contrary to assumption (i) above. Let us assume that $b_6^B, \ldots, b_9^B$ may still be taken to be negligible, but b_5^B need not be. Then (5.3) has to be evaluated at $b_6^B = b_7^B = b_8^B = b_9^B = 0$.

Let us consider the case of double collisions in which particles 2 and 3 collide first, followed by a collision of particles 3 and 1. The intermediate velocity of particle 3 is then given by

$$\vec{v}_3'' = \vec{p}_3''/m_3 = (\vec{K}^0 - \vec{p}_1^0 - \vec{p}_2')/m_3 , \tag{5.10}$$

if $\vec{p}_2'$ is the final momentum of particle 2. The beams of particles 2 and 3 must intersect in order for collisions to occur. If we call the time at which the (2, 3) collision takes place $t=0$ and its location $\vec{x}$, then

$$\vec{x}_2 = \vec{x} + t\vec{v}_2^0 , \tag{5.11}$$

$$\vec{x}_3 = \vec{x} + t\vec{v}_3^0 . \tag{5.12}$$

Let t_c be the time at which the collision of particle 3 with particle 1 occurs. Then we must have

$$\vec{x}_1 = \vec{x} + t\vec{v}_1^0 + t_c \vec{\Gamma} , \tag{5.13}$$

with

$$\vec{\Gamma} = \vec{v}_3'' - \vec{v}_1^0 , \tag{5.14}$$

so that $\vec{x}_1 = \vec{x}_3$ for $t = t_c$.

The parameters for this case are calculated in Appendix E, with the results given in (E12) and

(E16). Thus b_5^B is proportional to the time interval t_c between the (2, 3) collision and the (1, 3) collision. Its maximal value is determined by the experimental configuration. If L is the dimension of the region of intersection of the three beams in the direction $\vec{v}_3''$, then

$$0 < b_5^B < \Gamma L/|v_3''| \equiv \Gamma T_c\,, \tag{5.15}$$

where T_c is the maximal value of t_c. Outside this region we assume that the beams are contained in pipes, and a particle that travels up one of them before its second collision cannot reach the detector.

The five coordinates $b_1^F, \ldots, b_5^B$ of (E12) and (E16) are such that

$$db_1^F \cdots db_5^B = \Gamma(2E^0)^{1/2} M^{3/2}\, d^3x\, dt\, dt_c\,, \tag{5.16}$$

in terms of the point $\vec{x}$ of the (2, 3) collision, the time t along the particle trajectories, and the interval t_c between the two collisions. We must now carry out the integral

$$\begin{aligned}\Big(\prod_i m_i\Big)^{3/2}\rho(b^B) &= \int d^4b^F \prod_i \rho^{(i)} \\ &= (2E^0)^{1/2} M^{3/2} \int d^3x\, dt \prod_i \rho^{(i)} \\ &= (2E^0)^{1/2} M^{3/2}\, T \int d^3x \prod_i \rho^{(i)}\,,\end{aligned} \tag{5.17}$$

under assumption (ii) above for long times T of beam intersection. The integration over the position of the first collision is complicated by the fact that it necessarily depends on the intercollision time t_c, that is, on b_5^B. When $b_5^B = 0$, then the entire volume of beam intersection is available to the first collision; when b_5^B has its maximal value, then the accessible volume has shrunk to zero. In general, the dependence of the accessible volume on the intercollision time will be a function of the direction of $\vec{v}_3''$.

As a special example we may take a case in which the region of beam intersection is approximately spherical, say of radius a. Then the volume available to double collisions with a vectorial distance $\vec{d}$ between them is independent of the (fixed) direction of $\vec{d}$. Its value is readily calculated to be

$$\tfrac{1}{12}\pi(2a-d)^2(4a+d)\,,$$

as compared to the volume

$$V_{\text{int}} = \tfrac{4}{3}\pi a^3\,.$$

Hence we may write

$$\rho(b^B) = (2E^0)^{1/2}\Big(\prod_i m_i\Big)^{-3/2} \times M^{3/2} T V_{\text{int}} S(t_c, \vec{v}_3'') \prod_i \rho^{(i)0}\,, \tag{5.18}$$

where in this instance

$$S(t_c, \vec{v}_3'') = (1 - d/2a)^2(1 + d/4a)\,, \tag{5.19}$$

with $d = t_c|\vec{v}_3''|$. For other shapes of the region of beam intersection the function S will be more complicated.

We must now calculate the probability P_b for double scattering into the cone C on the assumption that the initial wave packet is described by the normalized function $g(k)$, centered and sharply peaked at k_0 in momentum space and at b in coordinate space:

$$P_b = (2\pi)^2 \int_C d^9k' \left| \int d^9k\, g(k) e^{-ib\cdot k}\, T(k', k) \times \delta^3(\vec{K} - \vec{K}')\, \hat{\delta}(E - E') \right|^2, \tag{5.20}$$

in a somewhat simplified notation.[25] The part of the T matrix of interest for double scattering is

$$T = \sum_{i \neq j} T_i G_0^+ T_j + \cdots,$$

where T_i and T_j are the T matrices for only two particles in interaction. In the momentum representation

$$G_0^+(E; k'', k''') = \delta^9(k'' - k''')(E + i\epsilon - E'')^{-1}\,.$$

We pick out a particular double scattering by the choice of the cone C. The absolute magnitude in (5.20) then contains

$$\cdots (E + i\epsilon - E'')^{-1} \cdots (E - i\epsilon - E''')^{-1} \cdots,$$

and for this product we utilize the result (D7) in the limit as $\epsilon \to 0$. The last term will not contribute, and the first term will give rise to the "true" 3-3 scattering as shown and discussed at length in Sec. IV. The term that clearly describes double scattering is the second. (Note the factor of 2, which would be absent if each Green's function had been separately written as a principal part plus an on-shell δ function.) Thus the probability relevant to double scattering is well approximated[26] by [say in the case of a (2, 3) collision followed by a (1, 3) collision]

$$P_b^{ds} = \int_C d^9k' |\, T_2(E_0; k', k_0'')\, T_1(E_0; k_0'', k_0)|^2 h_b(k')\,, \tag{5.21}$$

$$h_b = 8\pi^4 \int d^9k\, d^9\bar{k}\, g(k) g^*(\bar{k})\, e^{ib\cdot(\bar{k}-k)}$$
$$\times\, \delta^3(\vec{K}-\vec{K}')\, \delta^3(\vec{\bar{K}}-\vec{K}')\, \delta(E-E')$$
$$\times\, \delta(\bar{E}-E')\, \delta(E-E'')\, \delta(\bar{E}-\bar{E}''), \qquad (5.22)$$

because of the assumed sharp peaking of g at k_0. The notation here is such that k'' is the set of intermediate momenta determined by the double-scattering conditions:

$$\vec{p}_1 = \vec{p}_1'', \quad \vec{p}_2 + \vec{p}_3 = \vec{p}_2'' + \vec{p}_3'', \quad E = E'',$$
$$\vec{p}_2'' = \vec{p}_2', \quad \vec{p}_1'' + \vec{p}_3'' = \vec{p}_1' + \vec{p}_3', \quad E'' = E'. \qquad (5.23)$$

It is readily seen that for $k \simeq \bar{k} \simeq k_0$ we have

$$E'' - \bar{E}'' \simeq (\vec{p}_1 - \vec{\bar{p}}_1)\cdot(\vec{v}_1^{\,0} - \vec{v}_3^{\,\prime\prime}) = (\vec{\bar{p}}_1 - \vec{p}_1)\cdot\vec{\Gamma}, \qquad (5.24)$$

$\vec{\Gamma}$ being defined by (5.14). If the three vectors $\vec{v}_i$, $i=1,2,3$, are decomposed into components v_i^F, $i=1,\ldots,4$, v_i^B, $i=5,\ldots,9$, then the peaked nature of g leads to

$$\delta^4(v^F - \bar{v}^F) = (2E^0)^{1/2} M^{3/2} \delta^3(\vec{K} - \vec{\bar{K}})\, \delta(E-\bar{E}), \qquad (5.25)$$

as was shown in Ref. 10. Hence (5.22) becomes

$$h_b = 8\pi^4 M^{-3/2}(2E^0)^{-1/2}$$
$$\times \int d^9k\, d^9\bar{k}\, g(k) g^*(\bar{k})$$
$$\times\, e^{ib^B\cdot(\bar{v}^B - v^B)}\, \delta^3(\vec{K}-\vec{K}')\delta^4(v^F - \bar{v}^F)$$
$$\times\, \delta(\bar{E}-E')\delta(E-E'')\delta[\vec{\Gamma}\cdot(\vec{p}_1 - \vec{\bar{p}}_1)]. \qquad (5.26)$$

We now do the integration over $b_6^B, \ldots, b_9^B$, using the assumption (i a) above, and the fact that $\rho(b^B)$ is independent of these four components of b^B. Then, by (E10),

$$\int db_6^B \cdots db_9^B\, h_b = 32\pi^6 M^{-3/2}(2E^0)^{-1/2} \int d^9k\, d^9\bar{k}\, g(k) g^*(\bar{k})\, e^{ib_5^B(\bar{v}_5^B - v_5^B)}\, \delta^3(\vec{K}-\vec{K}')\delta(\bar{E}-E')\delta(E-E'')$$
$$\times\, \delta^4(v^F - \bar{v}^F)\delta(v_6^B - \bar{v}_6^B)\cdots\delta(v_9^B - \bar{v}_9^B)\delta(\Gamma(v_5^B - \bar{v}_5^B)). \qquad (5.27)$$

Use of (E11) converts the nine velocity δ functions into those for particle momenta, setting $k=\bar{k}$. The integrations over k and k' may now be done. Using the normalization of g to unity, we obtain

$$\int db_6^B \cdots db_9^B\, h_b = 32\pi^6 \left(\prod_i m_i\right)^{3/2} M^{-3/2}(2E^0)^{-1/2}\Gamma^{-1}$$
$$\times\, \delta^3(\vec{K}'-\vec{K}_0)\delta(E'-E_0)\delta(E''-E_0).$$

Consequently (5.18) leads to

$$\int d^5b^B \rho(b^B) h_b = 32\pi^6 \left(\prod_i \rho^{(i)0}\right)\delta^3(\vec{K}'-\vec{K}_0)\delta(E'-E_0)$$
$$\times\, \delta(E''-E_0) T V_{int} \bar{T}_c(\vec{v}_3''), \qquad (5.28)$$

where by (E16)

$$\bar{T}_c(\vec{v}_3'') = \Gamma^{-1}\int db_5^B\, S(t_c, \vec{v}_3'') = \int dt_c\, S(t_c, \vec{v}_3'') \qquad (5.29)$$

is a mean intercollision time. In the special instance of approximately spherical beam intersection, (5.19) leads to

$$\bar{T}_c(\vec{v}_3'') = \tfrac{3}{8} T_c, \qquad (5.30)$$

in which $T_c = 2a/|\vec{v}_3''|$ is the maximal value of t_c.

Insertion of (5.28) and (5.21) in (5.1) gives us the probability

$$P^{ds} = 32\pi^6 \left(\prod_i \rho^{(i)0}\right) T V_{int}$$
$$\times \int_C d^9k' \,|\, T_2(E_0; k', k_0'')\, T_1(E_0; k_0'', k_0)|^2\, \bar{T}_c(\vec{v}_3'')$$
$$\times\, \delta^3(\vec{K}'-\vec{K}_0)\delta(E'-E_0)\delta(E''-E_0). \qquad (5.31)$$

Hence if N_i particles of kind i, $i=1,2,3$, are sent in, then the number of triples of particles that can be expected to be found in cone C is $(\prod_i N_i)P$. If we set $d_i = \rho^{(i)0}N_i$, the particle density in the ith beam, then (5.31) implies a counting rate per unit time of

$$R = V_{int}\left(\prod_i d_i\right)\sigma_{ds}, \qquad (5.32)$$

where

$$\sigma_{ds} = 32\pi^6 \int_C d^9k' \,|\, T_2(E_0; k', k_0'')\, T_1(E_0; k_0'', k_0)|^2$$
$$\times\, \delta^3(\vec{K}'-\vec{K}_0)\delta(E'-E_0)\delta(E''-E_0)\, \bar{T}_c(\vec{v}_3'') \qquad (5.33)$$

is the specific double-scattering rate. It is the appearance of $\delta(E''-E_0)$ that puts the particles between collisions on the energy shell.

The specific three-particle scattering rates (5.9) and (5.33) have the dimensions (distance)^6/time, so that division by an initial velocity gives (distance)^5, the analog of (distance)^2 in the two-particle case. If the cone C is selected so that double scattering cannot occur for the final momenta in it, then E'' will be outside the region of integration and (5.33) vanishes. In that event the "true" 3-3 scattering (5.9) is all that is observed. However, if C includes double-scattering momenta, then (5.33) will generally be very much larger than (5.9). This is because of the appearance of $\overline{T}_c$, or of the intercollision distance $\overline{D}_c = \overline{T}_c|v_3''|$, which is *macroscopic*. In contrast, the distances that appear in (5.9) are all essentially the ranges of the interparticle forces or of their effects, and these are *microscopic*. It follows that *total* scattering rates, integrated over all final momenta, are always determined overwhelmingly by (5.33).

VI. FURTHER DISCUSSION

The results derived in Secs. IV and V allow us to calculate total double-scattering rates and total 3-3 rates without any appearance of infinities. As discussed at the end of Sec. V, in general the vast majority of 3-3 scattered particles are, in fact, double scattered, and the total double-scattering rate obtained by letting C become all of space and summing over all double-scattering pairs is for practical purposes identical to the total 3-3 rate. The total "true" 3-3 rate may be calculated by means of (4.10), but its observation is problematical and its interpretation is ambiguous owing to the appearance of the interference terms in (4.9), as these describe particles that are scattered *both* doubly and "truly" 3-3. The principal virtue of the result of Sec. IV consists therefore in rendering the expression (5.33) unambiguous [by justifying the use of (D7) in the derivation of (5.22)] and interpretable as a total 3-3 rate by demonstrating that the "true" 3-3 rate, including interference terms, is finite and, in fact, small compared to it.

Accelerators shooting three beams of particles at each other do not exist yet and are unlikely to be built in the near future. The calculated scattering rates therefore cannot be expected to be compared with experiment in the manner discussed for their derivation, now or soon. Nevertheless, total 3-3 scattering rates are not devoid of experimental significance. One of the important applications of three-particle collision probabilities lies in the calculation of third virial coefficients.[27] Our results make such calculations on a quantum-mechanical basis free from ambiguities.[27a]

A second area of application of three-particle collision probabilities is that of chemical reaction rates.[28] We are, in that case, of course, dealing with molecular rearrangement collisions, and the present paper deals only with elastic collisions of three particles. However, it is clear that our considerations are easily generalized to the scattering of three bound systems of particles giving rise to three other bound systems.[29] The only changes would be in the T-matrix elements, and in taking into account that the initial and final masses need not be the same. We may thus envisage two different kinds of processes.

The first rearrangement would be one that could take place by a two-step process. In the collision between molecules 1 and 2, a fragment A is transfered from 2 to 1 and fragment B from 1 to 2. In the second collision, between molecules 2 and 3, fragment C is transfered from 2 to 3, and D from 3 to 2. The final molecules are $1+A-B$, $2-A+B-C+D$, and $3+C-D$. The reaction rate for the three initial substances changing into the three final ones will be proportional to the total rate for the corresponding rearrangement collision, and this can be calculated by the appropriate generalization of (5.33).

The second kind of rearrangement is one that cannot occur in a two-step process. For example, suppose that in the reaction described above, fragment B does not have a bound state with $2-A$, but it does with $2-A+D-C$. Then the three-particle reaction can take place only via "true" 3-3 collisions. Its rate would be proportional to the "true" 3-3 scattering rate given by (4.10), appropriately generalized. How do we deal with the interference terms in that case?

It should be recognized that in such a case there will be no interference terms, nor will the original problem of infinities arise. If the reaction cannot go via a two-step process, this means that in the corresponding matrix elements of T, the $T_iG_0T_j$ terms vanish when G_0 goes on the energy shell. If they were present, the process could, in fact, go in two steps. Hence the (on-shell) double-scattering terms for this reaction are zero, and interferences cannot occur. Moreover, since the corresponding double-scattering matrix elements must vanish, at least as we approach the energy shell, the infinity in the differential rate, as we approach the double-scattering momenta, can also be expected to disappear.

APPENDIX A

The Jacobi coordinates of three particles in the center-of-mass system are defined here as in Ref. 4. Let the coordinates, momenta, and masses of the particles be $\vec{R}_i$, $\vec{p}_i$, and m_i, respectively, $i=1,2,3$. We set

$$\vec{r}_1 = (2\mu_1)^{1/2}(\vec{R}_2 - \vec{R}_3)\,,$$

$$\vec{\rho}_1 = (2/\overline{\mu}_1)^{1/2}(m_2\vec{R}_2 + m_3\vec{R}_3) = m_1(2/\overline{\mu}_1)^{1/2}\vec{R}_1\,, \qquad \text{(A1)}$$

$$\vec{k}_1 = (2\overline{\mu}_1)^{-1/2}\vec{p}_1\,, \quad \vec{q}_1 = (\tfrac{1}{2}\mu_1)^{1/2}(\vec{p}_2/m_2 - \vec{p}_3/m_3)\,,$$

$$\mu_1 = m_2 m_3/(m_2+m_3)\,, \quad \bar{\mu}_1 = m_1(m_2+m_3)/M\,,$$
$$M = m_1+m_2+m_3\,,$$

and cyclic permutations. A change from $\vec{r}_i, \vec{\rho}_i$ to $\vec{r}_j, \vec{\rho}_j$ is accomplished by the rotation

$$\vec{r}_j = a_{ji}\vec{r}_i + b_{ji}\vec{\rho}_i\,, \quad \vec{\rho}_j = -b_{ji}\vec{r}_i + a_{ji}\vec{\rho}_i\,, \tag{A2}$$

where

$$a_{ij} = a_{ji} = -(\mu_i\mu_j)^{1/2}/m_k\,, \quad k \neq i \neq j$$
$$-b_{ij} = b_{ji} = (\mu_j/\bar{\mu}_i)^{1/2}\,, \quad i,j = 1,2;2,3;3,1\,. \tag{A3}$$

Further relations are given in Ref. 4.

APPENDIX B

Using q_j'' as variable of integration transforms (3.2) to

$$\frac{1}{\rho_i}\xi_{ij} = \frac{ib_{ji}}{2\pi}\int d^3q_j''\,\frac{h_{ij}\exp\{i[(E-k_i''^2)^{1/2}r_i + a_{ji}\vec{k}_j\cdot\vec{\rho}_i + b_{ji}\vec{q}_j''\cdot\vec{\rho}_i]\}}{q_j''^2 - q_j^2 - i\epsilon}\,. \tag{B1}$$

We choose the direction of $\vec{\rho}_i$ as the z axis and denote the polar angles of $\vec{k}_j$ by θ and φ, and those of q_j'' by θ'' and φ''. The φ'' integration is done first, and the stationary-phase method yields

$$\frac{1}{\rho_i}\xi_{ij} \simeq \frac{i}{(2\pi)^{1/2}r_i^{1/2}}\,\frac{b_{ij}}{(a_{ij}|b_{ij}|k_j|\sin\theta|)^{1/2}}$$
$$\times\int_0^\infty dq_j''\,q_j''^{3/2}\int_{-\pi}^{\pi}\frac{d\theta''\sin\theta'' h_{ij}}{|\sin\theta''|^{1/2}}\,\frac{(E-k_i''^2)^{1/2}\exp[ig + \tfrac{1}{4}i\pi\,\mathrm{sgn}(b_{ij}\sin\theta\sin\theta'') + ia_{ij}\vec{k}_j\cdot\vec{\rho}_i]}{q_j''^2 - q_j^2 - i\epsilon}\,,$$

where

$$g = r_i(E-k_i''^2)^{1/2} + b_{ji}\rho_i q_j''\cos\theta''\,.$$

The θ'' integration, which originally extended from 0 to π, has been extended to $-\pi$ in order to take into account both stationary points at $\varphi''=\varphi$ and $\varphi''=\varphi+\pi$.

Next we perform the θ'' integration by the stationary-phase method. This will define a stationary point $\theta''=\theta_s$ at which

$$\left.\frac{\partial g}{\partial\theta''}\right|_{\theta''=\theta_s} = 0\,.$$

It establishes a relation between θ_s and γ, at fixed q_j'', given by

$$\gamma\sin\theta_s = a_{ij}k_j\sin(\theta_s-\theta)/(E-k_i''^2)^{1/2}\,, \tag{B2}$$

where

$$E - k_i''^2 = E - a_{ij}^2k_j^2 - b_{ij}^2q_j''^2 + 2a_{ij}b_{ij}k_jq_j''\cos(\theta_s-\theta)\,. \tag{B3}$$

The q_j'' integration is done next. If we denote by q_{js} the point at which g (at $\theta''=\theta_s$) is stationary with respect to q_j'', then the equation for q_{js} is

$$\gamma\cos\theta_s = \frac{a_{ij}k_j\cos(\theta_s-\theta) - b_{ij}q_{js}}{(E-k_{is}^2)^{1/2}}\,, \tag{B4}$$

where k_{is} is obtained by substituting $q_j''=q_{js}$ in (B3). The sum of the squares of (B2) and (B4) gives the result

$$(E-k_{is}^2)^{1/2} = K(1+\gamma^2)^{-1/2}\,. \tag{B5}$$

On the other hand, insertion of the ratio of (B2) and (B4) in the latter gives

$$b_{ij}q_{js} = a_{ij}k_j\sin\theta/\sin\theta_s\,, \tag{B6}$$

from which it follows that

$$b_{ij}\sin\theta\sin\theta_s < 0\,, \tag{B7}$$

since $a_{ij}<0$ and $q_{js}>0$. Use of (B6) in (B2) and (B4) also yields

$$\gamma^2 = \frac{a_{ij}^2k_j^2\sin^2(\theta_s-\theta)}{E\sin^2\theta_s - a_{ij}^2k_j^2\sin^2(\theta_s-\theta)} \tag{B8}$$

or

$$\gamma/(1+\gamma^2)^{1/2} = a_{ij}k_j\sin(\theta_s-\theta)/K\sin\theta_s\,. \tag{B8$'$}$$

Note that the stationary-phase evaluation of the θ'' integral makes θ_s a function of q_j'', and this dependence of θ_s on q_j'' has to be taken into account in the evaluation of the q_j'' integral by the stationary-phase method.

The presence of a pole at $q_j''=q_j+i\epsilon$ complicates the q_j'' integral. We use the the stationary-phase evaluations of such integrals given by Bleistein.[12,30] The result depends on whether the point q_{js} of stationarity coincides with the pole position q_j (in the limit as $\epsilon\to 0+$), is near it, or is far away from it. The coincidence of q_{js} with q_j defines the double-scattering direction in 6-space, i.e., the ridge. We obtain the following:

$$\frac{1}{\rho_i}\xi_{ij} = \frac{(\frac{1}{2}\pi)^{1/2}Ke^{i\pi/4}e^{iKR}}{|b_{ij}|q_j''R}\Gamma_{ij} + o(R^{-3/2})\,, \tag{B9}$$

where on the ridge

$$\Gamma_{ij} = (\tfrac{1}{2}\pi)^{1/2}e^{i\pi/4}\nu h_{ij} + O(R^{-1/2})\,; \tag{B10a}$$

near the ridge

$$\Gamma_{ij}=\left((2\pi)^{1/2}h_{ij}e^{i\pi/4}e^{-ia^2x^2/2}\theta(x) - h_{ij}\,\mathrm{sgn}x\,F(a|x|)-\frac{i}{a}\frac{\partial h_{ij}}{\partial q_j''}\right)\nu\,; \qquad \text{(B10b)}$$

off the ridge

$$\Gamma_{ij}=\left((2\pi)^{1/2}\nu h_{ij}e^{i\pi/4}\theta(x)e^{i(r_iq_i^d+\vec{\rho}_i\cdot\vec{k}_i^d)-iKR} + \frac{2iK^{1/2}h_{ij}(q_{js})q_{js}}{|b_{ij}|(1+\gamma^2)^{1/2}R^{1/2}(q_j^2-q_{js}^2)}\right), \qquad \text{(B10c)}$$

with

$$\nu=(1+\gamma^2\sin^2\theta_s)^{-1/2}\quad (q_j''=q_{js})\,, \qquad \text{(B11)}$$
$$a=\nu K^{-1/2}R^{1/2}|b_{ij}|(1+\gamma^2)^{1/2}\,,\quad x=q_{js}-q_j\,,$$

$$F(x)=\int_x^\infty dt\,e^{i(t^2-x^2)/2}\,,\quad \theta(x)=\tfrac{1}{2}(1+\mathrm{sgn}x)\,, \qquad \text{(B12)}$$

and $h_{ij}=h_{ij}(q_j''=q_j)$. Both $h_{ij}(q_{js})$ and h_{ij} are evaluated at $\varphi''=0$ and $\theta''=\theta_s$. Note the limiting values of the Fresnel function,

$$F(x)=ix^{-1}+O(x^{-3})\,,\quad \text{as } x\to\infty\,, \qquad \text{(B13)}$$

$$F(0)=(\tfrac{1}{2}\pi)^{1/2}e^{i\pi/4}\,. \qquad \text{(B14)}$$

q_i^d and $\vec{k}_i^d$ are the double-scattering values of q_i' and $\vec{k}_i'$, i.e., those obtained from (2.9).

It should be noted that the near-ridge value continuously goes over into the on-ridge value as $x\to 0$ (where only the leading term in $R^{-1/2}$ is kept), and that, similarly, the near-ridge value goes over continuously into the off-ridge value as $R\to\infty$ at fixed small x. Note also that the off-ridge value does *not* continuously go over into the on-ridge value as $x\to 0$. The nonuniform behavior of the wave function with respect to $x\to 0$ and $R\to\infty$ is contained in the Fresnel function, whose argument is a multiple of $|x|R^{1/2}$.

APPENDIX C

The near-ridge value of $\psi^{(ij)}$ is given in (3.8). It consists of three terms:

$$C_1=c_1e^{-ia^2x^2/2}\theta(x)\,. \qquad \text{(C1)}$$

$$C_2=c_2\,\mathrm{sgn}x\,F(a|x|)\,, \qquad \text{(C2)}$$

$$C_3=c_3a^{-1}\,, \qquad \text{(C3)}$$

where $a=cR^{1/2}$, c, c_1, c_2, and c_3 are constants, and F is given by (B12). In addition there are, of course, the remaining terms in $\psi_3+\psi_4$, which are continuous at $x=0$. Among them there will be terms from other double scatterings, which are $O(1)$, and other terms, $O(R^{-1/2})$. As explained in Sec. IV we shall ignore the double-scattering terms except near their own ridge, because off their ridge they are physically distinguishable from the remainder. Therefore we shall consistently put the remaining terms in the form

$$C_4=c_4R^{-1/2}\,. \qquad \text{(C4)}$$

Thus we must evaluate

$$I=\int_{-\epsilon}^{\epsilon}dx\,|C_1+C_2+C_3+C_4|^2\,, \qquad \text{(C5)}$$

keeping terms of order R^{-1} or larger. In the ordering of terms we must remember (4.6) and (4.8). By (4.5)

$$\int_{-\epsilon}^{\epsilon}dx\,|C_1|^2=|c_1|^2\epsilon\,. \qquad \text{(C6)}$$

Integration by parts shows that

$$\int_0^{\epsilon}dx\int_{ax}^{\infty}ds\,e^{-is^2/2}=-ia^{-1}+o(a^{-1})\,,$$

and hence

$$\int_{-\epsilon}^{\epsilon}dx\,C_1C_2^*=-ic_1c_2^*a^{-1}+o(R^{-1/2})\,. \qquad \text{(C7)}$$

Because C_2 is an odd function of x,

$$\int_{-\epsilon}^{\epsilon}dx\,C_2C_3^*=\int_{-\epsilon}^{\epsilon}dx\,C_2C_4^*=0\,. \qquad \text{(C8)}$$

It is clear that

$$\int_{-\epsilon}^{\epsilon}dx\,|C_3+C_4|^2=O(\epsilon R^{-1}) \qquad \text{(C9)}$$

and hence is negligible.

We readily find that

$$\int_{-\epsilon}^{\epsilon}dx\,\theta(x)e^{ia^2x^2/2}=(\tfrac{1}{2}\pi)^{1/2}e^{i\pi/4}a^{-1}+o(a^{-1})\,,$$

and therefore

$$\int_{-\epsilon}^{\epsilon}dx\,C_1^*C_3=(\tfrac{1}{2}\pi)^{1/2}e^{i\pi/4}c_1^*c_3a^{-2}+o(R^{-1})\,, \qquad \text{(C10)}$$

and similarly

$$\int_{-\epsilon}^{\epsilon}dx\,C_1^*C_4=(\tfrac{1}{2}\pi)^{1/2}e^{i\pi/4}c_1^*c_4a^{-1}R^{-1/2}+o(R^{-1})\,. \qquad \text{(C11)}$$

The only term left to be considered is of the form

$$\int_{-\epsilon}^{\epsilon}dx\,|F(a|x|)|^2=2\epsilon|F(a\epsilon)|^2-4a^{-1}\,\mathrm{Im}F(a\epsilon)+2\pi^{1/2}a^{-1}\,,$$

by integration by parts. The asymptotic value (B13) yields

$$\int_{-\epsilon}^{\epsilon}dx\,|F(a|x|)|^2=2\pi^{1/2}a^{-1}-2a^{-2}\epsilon^{-1}+O(a^{-4}\epsilon^{-3})\,.$$

Using (4.8) we have

$$\int_{-\epsilon}^{\epsilon} dx\, |C_2|^2 = 2\pi^{1/2}|c_2|^2 a^{-1} - 2|c_2|^2 a^{-2}\epsilon^{-1} + o(R^{-1})\,. \tag{C12}$$

As a result of (C6)–(C12), the integral (C5) becomes

$$I = |c_1|^2\epsilon + 2\,\mathrm{Re}[c_2^*(\pi^{1/2}c_2 - ic_1)]a^{-1} - 2|c_2|^2 a^{-2}\epsilon^{-1} + (2\pi)^{1/2}\,\mathrm{Re}[e^{i\pi/4}c_1^*(c_3 a^{-2} + c_4 a^{-1}R^{-1/2})] + o(R^{-1})\,. \tag{C13}$$

The values of the constants, given by comparison of (3.8) with (C1)–(C3), are

$$c_1 = \delta(2\pi)^{1/2}h_{ij}e^{i\pi/4}q_j\,,\quad c_2 = -\delta h_{ij}q_j\,,\quad c_3 = -i\delta\frac{\partial h_{ij}}{\partial q_j''}q_j\,, \tag{C14}$$

where δ is given by (3.9). Consequently

$$\pi^{1/2}c_2 - ic_1 = i\pi^{1/2}c_2\,,$$

and the second term in (C13) vanishes. This is the interference term, which in the integral of $|\psi|^2$ is of order $R^{-9/2}$. We are thus left with terms of order R^{-4} and of order R^{-5} only:

$$I = |\delta|^2 q_j^2\Big[2\pi|h_{ij}|^2\epsilon - 2|h_{ij}|^2 c^{-2}\epsilon^{-1}R^{-1} + 2\pi c^{-2}R^{-1}\,\mathrm{Im}\Big(h_{ij}^*\frac{\partial h_{ij}}{\partial q_j''}\Big) + 2\pi c^{-1}R^{-1}\,\mathrm{Re}(h_{ij}^*c_4)\Big] + o(R^{-1})\,, \tag{C15}$$

where

$$c = \nu K^{-1/2}|b_{ij}|(1+\gamma^2)^{1/2}\,,$$

ν being defined in (B11), and all constants are evaluated on the ridge.

We next evaluate the integrals away from the ridge, using the off-ridge value given in (3.8) and, for reasons explained in Sec. IV, discarding the first term. The integrand is of the following form:

$$J = \int dx\, |C_5(q_j^2 - q_{js}^2)^{-1} + C_6|^2 R^{-1}\,,$$

with the interval $-\epsilon < x < \epsilon$ omitted. Here, of course, C_5 and C_6 are not constants. Now according to Appendix D

$$\Big(\int^{-\epsilon} + \int_{\epsilon}\Big)dx\,[|C_5|^2(q_j^2 - q_{js}^2)^{-2} + |C_6|^2 + 2\,\mathrm{Re}(C_5^*C_6)(q_j^2 - q_{js}^2)^{-1}]$$
$$= \mathcal{P}\int dx\,|C_5|^2(q_j^2 - q_{js}^2)^{-2} + \int dx\,|C_6|^2 + \mathcal{P}\int dx\, 2\,\mathrm{Re}(C_5^* - C_6)(q_j^2 - q_{js}^2)^{-1} + \frac{\epsilon^{-1}|C_5|^2}{2}\Big|_{x=0} q_j^{-2} + o(1)\,,$$

and hence

$$J = R^{-1}\mathcal{P}\int dx\,|C_5(q_j^2 - q^2{}_{js})^{-1} + C_6|^2 + \frac{\epsilon^{-1}R^{-1}|C_5|^2}{2}\Big|_{x=0} q_j^{-2} + o(R^{-1})\,. \tag{C16}$$

Examination of the constants shows that

$$|C_5|^2\Big|_{x=0} = 4q_j^4 c^{-2}|h_{ij}|^2|\delta|^2\,,$$

and hence, when I and J are added, the two terms of order $\epsilon^{-1}R^{-1}$ cancel:

$$I + J = 2\pi|\delta|^2 q_j^2|h_{ij}|^2\epsilon + 2\pi q_j^2|\delta|^2 c^{-2}\,\mathrm{Im}\Big(h_{ij}^*\frac{\partial h_{ij}}{\partial q_j''}\Big)R^{-1} + 2\pi q_j^2|\delta|^2 c^{-1}\,\mathrm{Re}(h_{ij}^*C_4)R^{-1} + R^{-1}\mathcal{P}\int dq_{js}\,|C_5(q_j^2 - q_{js}^2)^{-1} + C_6|^2 + o(R^{-1})\,. \tag{C17}$$

APPENDIX D

We define here the principal value of an integral whose integrand has a pole of second order. Assume that in the domain $a \le x \le b$ the functions $f(x)$ and $g(x)$ are continuous and differentiable. For $a < x_0 < b$ let $g(x_0) = 0$ and $g'(x_0) \ne 0$. Then we define

$$\mathcal{P}\int_a^b dx\,\frac{f(x)}{g^2(x)} = \lim_{\eta\to 0}\int_a^b dx\, f(x)\,\frac{1}{2}\Big(\frac{1}{[g(x)+i\eta]^2} + \frac{1}{[g(x)-i\eta]^2}\Big)\,. \tag{D1}$$

Under the stated assumptions we obtain, integrating by parts,

$$\int_a^b dx\, f(x)\frac{1}{2}\left(\frac{1}{(g+i\eta)^2}+\frac{1}{(g-i\eta)^2}\right)=f(a)\frac{1}{2}\left(\frac{1}{g(a)+i\eta}+\frac{1}{g(a)-i\eta}\right)-f(b)\frac{1}{2}\left(\frac{1}{g(b)+i\eta}+\frac{1}{g(b)-i\eta}\right)$$

$$+\int_a^b dx\, f'(x)\frac{1}{2}\left(\frac{1}{g+i\eta}+\frac{1}{g-i\eta}\right)-\frac{f(a)}{g(a)}-\frac{f(b)}{g(b)}+\mathcal{P}\int_a^b dx\,\frac{f'(x)}{g(x)},$$

where the right-hand side now contains the usual well-known Cauchy principal value. Hence the limit exists and we have

$$\mathcal{P}\int_a^b dx\,\frac{f(x)}{g^2(x)}=\frac{f(a)}{g(a)}-\frac{f(b)}{g(b)}+\mathcal{P}\int_a^b dx\,\frac{f'(x)}{g(x)}. \tag{D2}$$

The principal value may also be written as follows:

$$\left(\int_a^{x_0-\epsilon}+\int_{x_0+\epsilon}^b\right)dx\,\frac{f(x)}{g^2(x)}=\left(\int_a^{x_0-\epsilon}+\int_{x_0+\epsilon}^b\right)\frac{dx}{(x-x_0)^2}\left(\frac{f(x)(x-x_0)^2}{g^2(x)}\right)$$

$$=\frac{f(a)}{g^2(a)}(a-x_0)-\frac{f(b)}{g^2(b)}(b-x_0)+\frac{2}{\epsilon}\,\frac{f(x_0)}{[g'(x_0)]^2}+\left(\int_a^{x_0-\epsilon}+\int_{x_0+\epsilon}^b\right)\frac{dx}{x-x_0}\,\frac{d}{dx}\left(\frac{f(x)(x-x_0)^2}{g^2(x)}\right).$$

Consequently

$$\lim_{\epsilon\to 0^+}\left[\left(\int_a^{x_0-\epsilon}+\int_{x_0+\epsilon}^b\right)dx\,\frac{f(x)}{g^2(x)}-\frac{2}{\epsilon}\,\frac{f(x_0)}{[g'(x_0)]^2}\right]=\frac{f(a)(a-x_0)}{g^2(a)}-\frac{f(b)(b-x_0)}{g^2(b)}+\mathcal{P}\int_a^b\frac{dx}{x-x_0}\,\frac{d}{dx}\left(\frac{f(x)(x-x_0)^2}{g^2(x)}\right).$$

We now rewrite the principal value on the right-hand side,

$$\mathcal{P}\int_a^b\frac{dx}{x-x_0}\,\frac{d}{dx}\left(\frac{f(x)(x-x_0)^2}{g^2(x)}\right)=\lim_{\eta\to 0}\int_a^b dx\,\frac{d}{dx}\left(\frac{f(x-x_0)^2}{g^2}\right)\frac{1}{2}\left(\frac{1}{x-x_0+i\eta}+\frac{1}{x-x_0-i\eta}\right)$$

$$=\frac{f(b)(b-x_0)}{g^2(b)}-\frac{f(a)(a-x_0)}{g^2(a)}+\lim\int_a^b dx\,\frac{1}{2}\left(\frac{1}{(x-x_0+i\eta)^2}+\frac{1}{(x-x_0-i\eta)^2}\right)\frac{f(x)(x-x_0)^2}{g^2(x)}.$$

Now

$$\frac{x-x_0}{g(x)}\,\frac{1}{x-x_0+i\eta}=\frac{1}{g(x)+i\eta h(x)},$$

where

$$h(x)=g(x)/(x-x_0),$$

which, near $x=x_0$, has a fixed sign. Hence

$$\lim_{\eta\to 0}\int_a^b dx\,\frac{1}{2}\left(\frac{1}{(x-x_0+i\eta)^2}+\frac{1}{(x-x_0-i\eta)^2}\right)\frac{f(x)(x-x_0)^2}{g^2(x)}=\lim_{\eta\to 0}\int_a^b dx\, f(x)\frac{1}{2}\left(\frac{1}{[g(x)+i\eta]^2}+\frac{1}{[g(x)-i\eta]^2}\right).$$

Therefore

$$\mathcal{P}\int_a^b dx\,\frac{f(x)}{g^2(x)}=\lim_{\epsilon\to 0^+}\left[\left(\int_a^{x_0-\epsilon}+\int_{x_0+\epsilon}^b\right)dx\,\frac{f(x)}{g^2(x)}-\frac{2}{\epsilon}\,\frac{f(x_0)}{[g'(x_0)]^2}\right]. \tag{D3}$$

Let us combine the two terms in the large parentheses in (D1):

$$\mathcal{P}\int_a^b dx\,\frac{f(x)}{g^2(x)}=\lim_{\eta\to 0}\int_a^b dx\, f(x)\,\frac{g^2-\eta^2}{(g^2+\eta^2)^2}. \tag{D4}$$

This shows explicitly that the definition (D1) is not to be confused with the limit of

$$\int dx\,\frac{f(x)}{|g+i\eta|^2},$$

which generally does not exist.

It should be emphasized that for $f(x)\geqslant 0$, the principal value defined in (D1) is not necessarily positive! One easily calculates, for example, that

$$\mathcal{P}\int_{-1}^1\frac{dx}{x^2}=-2. \tag{D5}$$

These principal values therefore have a certain counterintuitive aspect.

In a manner analogous to (D1) we also define

$$\mathcal{P}\frac{1}{xy}=\tfrac{1}{2}\lim_{\epsilon\to 0}\left(\frac{1}{x+i\epsilon}\,\frac{1}{y+i\epsilon}+\frac{1}{x-i\epsilon}\,\frac{1}{y-i\epsilon}\right). \tag{D6}$$

One then readily finds that

$$\lim_{\epsilon\to 0^+}\frac{1}{x-i\epsilon}\frac{1}{y+i\epsilon}=\mathcal{P}\frac{1}{xy}+2\pi^2\delta(x)\delta(y)+i\pi\left(\delta(x)\mathcal{P}\frac{1}{y}-\delta(y)\mathcal{P}\frac{1}{x}\right). \tag{D7}$$

APPENDIX E

Let $\vec{p}_i^{\,0}$ be the particle momenta at the center of the wave packet; then

$$\vec{K}^0=\sum_{i=1}^{3}\vec{p}_i^{\,0}, \tag{E1}$$

the total (central) momentum;

$$\vec{v}_i^{\,0}=\vec{p}_i^{\,0}/m_i, \tag{E2}$$

the (central) particle velocities;

$$\vec{V}_i^0=\vec{v}_i^{\,0}-\vec{K}^0/M, \tag{E3}$$

the (central) particle velocities relative to the center of mass; and

$$E^0=\sum_{i=1}^{3}\frac{\vec{p}_i^{\,02}}{2m_i}-\frac{\vec{K}^{02}}{2M}=\sum_{i=1}^{3}\frac{m_i\vec{V}_i^{02}}{2}, \tag{E4}$$

the (central) energy in the center-of-mass system.

If $\vec{y}_i$, $i=1,2,3$, is any set of three vectors, then, as in Ref. 10, we define $\bar{y}_i$, $i=1,2,3$, as the three components of

$$\vec{\bar{y}}=M^{-1/2}\sum_{i=1}^{3}m_i\vec{y}_i \tag{E5}$$

and

$$\bar{y}_4=(2E^0)^{-1/2}\sum_{i=1}^{3}m_i\vec{y}_i\cdot\vec{V}_i^0. \tag{E6}$$

If the 27 vectors $\vec{a}_{ij}$, $i=1,2,3$, $j=1,\ldots,9$, are such that

$$\sum_{i=1}^{3}m_i\vec{a}_{ij}=\sum_{i=1}^{3}m_i\vec{a}_{ij}\cdot\vec{V}_i^0=0, \tag{E7}$$

then we can write

$$\vec{y}_i=M^{-1/2}\vec{\bar{y}}+(2E^0)^{-1/2}\vec{V}_i^0\bar{y}_4+\sum_{j=1}^{9}\vec{a}_{ij}\bar{y}_j,\quad i=1,2,3, \tag{E8}$$

and[31]

$$\sum_{i=1}^{3}m_i\vec{y}_i^{\,2}=\sum_{i=1}^{9}\bar{y}_i^{\,2}, \tag{E9}$$

provided that

$$\sum_{i=1}^{3}m_i\vec{a}_{ij}\cdot\vec{a}_{il}=\delta_{jl},\quad j,l=1,\ldots,9,$$

which we shall always assume. It follows that

$$d^3y_1\,d^3y_2\,d^3y_3=\left(\prod_{i=1}^{3}m_i\right)^{-3/2}d^9\bar{y}, \tag{E10}$$

$$\delta^3(\vec{y}_1)\,\delta^3(\vec{y}_2)\,\delta^3(\vec{y}_3)=\left(\prod_{1}^{3}m_i\right)^{3/2}\delta^9(\bar{y}). \tag{E11}$$

We label the first four $\bar{y}_i=y_i^F$, $i=1,\ldots,4$, and the other five $\bar{y}_i=y_i^B$, $i=5,\ldots,9$.

If two particles with coordinates $\vec{x}_i$, $i=2,3$, at the time $t=0$ collide at $\vec{x}$ and at the time t_c particle 3 collides with particle 1, as in (5.11)–(5.13), then we easily calculate that

$$\begin{aligned}\vec{\bar{x}}&=M^{1/2}\vec{x}+M^{-1/2}\vec{K}^0t+t_c m_1M^{-1/2}\vec{\Gamma},\\ \bar{x}_4&=(2E^0)^{1/2}t+(2E^0)^{-1/2}m_1\vec{V}_1^0\cdot\vec{\Gamma}t_c,\end{aligned} \tag{E12}$$

$$\sum_{j=5}^{9}\vec{a}_{ij}\bar{x}_j=-t_c(\alpha\vec{V}_i^0+m_1M^{-1}\vec{\Gamma}-\vec{\Gamma}\delta_{1i}),\quad i=1,2,3, \tag{E13}$$

where $\vec{\Gamma}$ is given by (5.14) and

$$\alpha=(2E^0)^{-1}m_1\vec{V}_1^0\cdot\vec{\Gamma}. \tag{E14}$$

Since only five parameters are needed for the description of (5.11)–(5.13), namely, $\vec{x}$, t, and t_c, we set $\bar{x}_6=\cdots=\bar{x}_9=0$, so that

$$\sum_{j=5}^{9}\vec{a}_{ij}\bar{x}_j=\vec{a}_{i5}\bar{x}_5. \tag{E15}$$

$\bar{x}_5$ may be calculated from (E9):

$$\bar{x}_5=t_c\Gamma, \tag{E16}$$

where

$$\Gamma^2=[m_1(m_2+m_3)/M]\vec{\Gamma}^2-(m_1^2/2E^0)(\vec{V}_1^0\cdot\vec{\Gamma})^2. \tag{E17}$$

The five parameters $\bar{x}_i$, $i=1,\ldots,5$, are the five numbers we call b_i^F, $i=1,\ldots,4$ and b_5^B for the three beams described by (5.11)–(5.13).

Equation (E15), together with (E16) and (E13), allows us to conclude that

$$\Gamma\vec{a}_{i5}=-(\alpha\vec{V}_i^0+m_1M^{-1}\vec{\Gamma}-\vec{\Gamma}\delta_{i1}), \tag{E18}$$

and particularly, from (E17),

$$\vec{a}_{15}\cdot\vec{\Gamma}=\Gamma m_1^{-1}. \tag{E19}$$

It follows that if the set of vectors η_i, $i=1,2,3$, is such that $\eta_i^F=0$, $i=1,\ldots,4$, $\eta_i^B=0$, $i=6,\ldots,9$, then for the specific transformation implied by (5.11)–(5.13), we have

$$\vec{\eta}_1\cdot\vec{\Gamma}=\vec{a}_{15}\cdot\vec{\Gamma}v_5^B=\Gamma m_1^{-1}v_5^B. \tag{E20}$$

In the application of this result in (5.27) $\vec{\eta}_1=\vec{v}_1-\vec{\bar{v}}_1$ and all its components except the fifth vanish, because of the other δ functions in (5.27).

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†Present address: Dept. of Physics, Technion, Haifa, Israel.

[1]E. Gerjuoy, J. Phys. B 3, 92 (1970); and Philos. Trans. R. Soc. Lond. A 270, 197 (1971).

[2]J. Nuttall, J. Math. Phys. 12, 1896 (1971).

[3]S. P. Merkuriev, Teor. Mat. Fiz. 8, 235 (1971).

[4]R. G. Newton, Ann. Phys. (N.Y.) 74, 324 (1972); 78, 561 (1973).

[5]T. A. Osborn and D. Bollé, Phys. Rev. C 8, 1198 (1973).

[6]This is equivalent to saying that particle l, $l \neq i$, $l \neq j$, collides first with particle i and then with j.

[7]Our notation is always to denote the magnitude $|\vec{x}|$ of a vector $\vec{x}$ by x, and the unit vector $\vec{x}/x$ by $\hat{x}$.

[8]The rigorous general statement of this is the "scattering-into-cones" theorem; see J. D. Dollard, Commun. Math. Phys. 12, 193 (1969); J. Math. Phys. 14, 708 (1973); J. M. Jauch, R. Lavine, and R. G. Newton, Helv. Phys. Acta 45, 325 (1972).

[9]A discussion of the way in which it could be measured is to be found in Ref. 10.

[10]R. G. Newton and R. Shtokhamer, in *Physical Reality and Mathematical Description*, edited by C. P. Enz and J. Mehra (Reidel, Dordrecht, 1974), p. 286.

[11]Actually we use the result of Bleistein (Ref. 12), which differs somewhat from those of Nuttall (Ref. 2) and Merkuriev (Ref. 3). However, both contain the same Fresnel function.

[12]N. Bleistein, Commun. Pure Appl. Math. 19, 353 (1966).

[13]Equation (3.2) is obtained from (4.17) of Ref. 4 by evaluating Q_i there asymptotically. In all other respects (3.2) is still exact.

[14]These equations express a limited aspect of the double scattering of the pair j followed by that of the pair i. They do not put the intermediate state on the energy shell, though.

[15]It should be noted that the near-ridge result of (3.8) differs from those of Nuttall (Ref. 2) and Merkuriev (Ref. 3), because of our use of Ref. 12. The off-ridge result of (3.8) also differs from that of Ref. 4 in the absence of a bothersome factor $|\vec{k}_i' \cdot q_j''|$ in the denominator of the double-scattering term. This difference arises from a different evaluation of the angle integrals. Whereas one of the angle integrations was asymptotically evaluated in Ref. 4 by an integration by parts, it is now evaluated in App. B by the method of stationary phase. The previous integration by parts was incorrect as an asymptotic evaluation, because it gave rise to a double pole in the integrand of the remainder.

[16]Of course, we really need the flux across the hypersurface at R. However, the flux and the density differ only by a simple constant factor, because of the exponential form of the asymptotic wave function.

[17]The order of integrations is irrelevant, because of the positivity of the integrand.

[18]If the right-hand side of (4.3) is larger than K, then the domain of θ is restricted to those values which keep $q_{js} \leq K$.

[19]In the case of the scattering of a particle by a center, the interference terms resulting from this indistinguishability can be used for the derivation (Ref. 20) of an "extinction theorem," which, together with the conservation of particles, leads to the optical theorem. It would be tempting to pursue an analogous argument in the present situation. However, this path appears to lead to no tangible result, because of the absence of a conservation of 3-3 scattering.

[20]H. C. van de Hulst, Physica (Utr.) 15, 740 (1949).

[21]See (4.36) of Ref. 4.

[22]That P_b in fact has the requisite property of decrease for a certain class of interactions was shown by E. Campesino-Romeo and J. R. Taylor, J. Math. Phys. 16, 1227 (1975).

[23]The $\vec{p}_i^{\,0}$, $i=1,2,3$, are the particle momenta at the center of the wave packet.

[24]See Appendix E for definitions of the notation. Note particularly that $E_0 = \sum \vec{p}_i^{\,02}/2m_i$ is the energy at the center of the packet, and $E^0 = E_0 - \vec{K}^{02}/2M$ is the central energy in the center-of-mass system.

[25]We are here denoting the nine-dimensional vector made up of the particle momenta by k; $\vec{K}$ and E are the total momentum and energy, respectively.

[26]In the sense of sharp peaking of g, the sharper the peaking of g, the better the approximation.

[27]See, for example, G. E. Uhlenbeck and G. W. Ford, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1962), Vol. 1, Pt. B, Chap. III; J. D. Hirschfelder, C. G. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), Chap. 3. For a recent calculation see B. Jancovici and S. P. Merkuriev, Phys. Rev. A 12, 2610 (1975).

[27a]*Note added in proof.* This remark is based on classical analogy. There is, in fact, a history of quantum-mechanical derivations of expressions for the third virial coefficients of gases based on well-defined three-particle equations: A. S. Reiner, Phys. Rev. 151, 170 (1966); W. G. Gibson, Phys. Lett. 21, 619 (1966); B. J. Baumgartl, Z. Phys. 198, 148 (1967); D. Bedeaux, Physica (Utr.) 45, 469 (1970); S. Y. Larsen and P. L. Mascheroni, Phys. Rev. A 2, 1018 (1970). These papers, however, ignore the difficulties posed by double scattering. The following authors do take these problems into account: R. Dashen, S. Ma, and H. Bernstein, Phys. Rev. 187, 345 (1969); R. Dashen and S. Ma, J. Math. Phys. 11, 1136 (1970) and 12, 689 (1971); V. S. Buslaev and S. P. Merkuriev, Izv. Akad. Nauk SSSR, Theor. Mat. Phys. 5, 372 (1970); Trudy Mat. Inst. Steklov 110, 29 (1970) [(Proc. Steklov Inst. Math., Am. Math. Soc., 1972), p. 28]; Doklady Akad. Nauk SSSR 189, 269 (1969) [Sov. Phys.-Doklady 14, 1055 (1970)]. The last-mentioned paper appears to differ from other authors in that it contains additional terms in its result. See also T. A. Osborn and T. Y. Tsang (report of work prior to publication). It is clear from these works that neither (4.10) nor (5.33) directly enter into expressions for the third virial coefficient. The first of the interference terms in (4.9), on the other hand, is of a similar form as ubiquitous expressions in the virial coefficients.

[28]For an extensive discussion of the dependence of chemical reaction rates on triple collisions, see F. T. Smith, in *Kinetic Processes in Gases and Plasmas*, edited by A. R. Hochstim (Academic, New York, 1969), p. 321.

[29]Reference 10 already includes the treatment of such systems, away from the double-scattering ridges.

[30]Except for the correction of a sign error in the second term on the right-hand side of his Eq. (4.1). We note that as compared to the results of Refs. 2 and 3, Bleistein's contains an extra term which near the ridge becomes equal to the derivative of h_{ij}. This term is explicitly visible in (B10).

[31]The reason for using this particular metric is that on the one hand the Fourier transform of a wave packet centered at b contains the factor $\exp(i\sum_j \vec{b}_j\cdot\vec{p}_j)$, and on the other hand a vector should be orthogonal to the impact-parameter space if all of the particles are shifted in proportion to their velocities.