

# Some Fundamental Difficulties with Quantum Mechanical Collision Theory

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*When quantum scattering theory is applied strictly from the point of view that the state of a system is completely described by the density matrix, whether pure or mixed, it is not possible to assume that colliding particles are at all times individually in pure states. Exact results are significantly different from conventionally accepted approximations. In particular, it turns out that the cross section as ordinarily defined in the S-matrix formalism is an adequate parameter for deciding the outcome of interactions only when the particles are carefully prepared in matching pure states. In general the use of the cross section in studying pair collisions in a real gas is shown to be analogous to a repeated "collapse of the wave function" after each collision, and involves arbitrary removal of nondiagonal elements of the density matrix, thus violating the basic laws of quantum dynamical evolution.*

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## 1. INTRODUCTION

As Goldberger and Watson state in the Preface to their authoritative monograph on collision theory,<sup>(1)</sup> it is generally agreed that to describe particle collisions one should prepare both projectile and target particle in wave packets aimed at each other and watch them evolve according to the standard time evolution formula of quantum mechanics. Like all treatises on quantum scattering, their work was concerned with the calculation of differential cross sections under a variety of circumstances, and they eventually introduced standard formal techniques, but only after assuring themselves "that there are no serious conceptual problems involved."

In this paper we investigate a conceptual problem in quantal collision theory that has evidently escaped general notice, presumably because it is

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possible to ignore it if one is only interested in scattering cross sections. It does, however, have a deep significance for such questions as the role of molecular collisions in the dynamical behavior of a gas not in thermal equilibrium.

The first point is briefly the following: while the transformation from two actual particles ( $A, B$ ) to the two fictitious particles, center of mass ( $C$ ) and reduced mass ( $R$ ), certainly reduces the two-body problem to two one-body problems in classical theory, the separation is not complete when quantum mechanical wave packets are involved, except under special conditions, which we shall describe.

The second point: a pair of particles prepared for a collision in arbitrary individual pure states will not, in general, after the collision, asymptotically approach individual pure states, although the overall pair state of course remains pure. Under these circumstances it is easy to show that the scattering cross section, as defined in the  $S$ -matrix formalism, is not an adequate parameter for precisely determining the result of the interaction.

This situation becomes more evident in terms of Hilbert space concepts. Let  $\mathcal{H}_A, \mathcal{H}_B$  be the Hilbert spaces appropriate for the two actual particles, whose Hamiltonian includes an interaction operator that acts on the tensor product space  $\mathcal{H}_A \otimes \mathcal{H}_B$ . Going over to the description in terms of "quasi-particles"  $R$  and  $C$  separates the Hamiltonian into  $H_C$  and  $H_R$  operating in two Hilbert spaces  $\mathcal{H}_C$  and  $\mathcal{H}_R$  which constitute a refactoring of the global Hilbert space

$$\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B = \mathcal{H}_C \otimes \mathcal{H}_R \quad (1)$$

Here  $H_R$  contains the potential for quasiparticle  $R$ , and  $H_C$  is a free-particle Hamiltonian for the quasiparticle  $C$ . Now the  $AB$  pair may be prepared in separate pure wave packets, and this state would be represented by a statistical operator (density matrix) that is factorizable:

$$\rho_{AB} = \rho_A \otimes \rho_B \quad (2)$$

This means that the two particles are initially uncorrelated, and their states  $\rho_A, \rho_B$  are pure projection operators in the spaces  $\mathcal{H}_A, \mathcal{H}_B$ , respectively. In going over to the  $CR$  picture, the equality

$$\rho_{AB} = \rho_{CR} \quad (3)$$

induces a well-defined change in the appearance of the statistical operator, but it is in general not true that  $\rho_{CR}$  can be factorized into operators in the spaces  $\mathcal{H}_C$  and  $\mathcal{H}_R$ ; i.e.,

$$\rho_{AB} = \rho_{CR} \neq \rho_C \otimes \rho_R \quad (4)$$

To determine the reduced statistical operators for the individual quasiparticles, one has to take the partial traces:

$$\rho_C = \text{Tr}_R \rho_{CR}, \quad \rho_R = \text{Tr}_C \rho_{CR} \quad (5)$$

While the operator  $\rho_{AB}$  ( $=\rho_{CR}$ ) is a pure projection operator in the example contemplated above, neither  $\rho_R$  nor  $\rho_C$  as defined in Eq. (5) need be pure—in general they are not. Thus while the collision would not change the purity of the state of the pair as a whole, a mistaken interpretation of the parts played by  $\rho_R$  and  $\rho_C$  in the quasiparticle problem could lead one to suppose that the collision had caused a transition from a pure state to a mixed one.

We shall give a clear example of this peculiar behavior of wave packets in the  $CR$  picture, and discuss its significance both for collision theory and for the larger question of thermodynamic irreversibility.

## 2. MINIMUM UNCERTAINTY PACKETS

To establish the formalism, we discuss the standard minimum uncertainty wave packet for a single free particle, which is given in the Schrödinger representation by the normalized wave function

$$\psi(\mathbf{q}) = (2\pi\Delta q^2)^{-3/4} \exp[-(\mathbf{q} - \langle \mathbf{q} \rangle)^2 / (4\Delta q^2) + i\mathbf{q} \cdot \langle \mathbf{p} \rangle] \quad (6)$$

where  $\mathbf{q}$  is the position vector,  $\langle \mathbf{q} \rangle$  is the mean position,  $\langle \mathbf{p} \rangle$  is the mean momentum,  $\Delta q^2$  is the common dispersion in each of the three Cartesian dimensions of space, and  $\hbar = 1$ .

In the Dirac notation we have the scalar product

$$\langle \mathbf{q} | \mathbf{p} \rangle = (2\pi)^{-3/2} \exp(i\mathbf{q} \cdot \mathbf{p}) \quad (7)$$

and we shall wish to write the wave function  $\psi(\mathbf{q})$  in the form

$$\psi(\mathbf{q}) = \langle \mathbf{q} | A \rangle \quad (8)$$

where  $|A\rangle$  is the Hilbert unit vector represented by the wave packet. The statistical operator  $\rho$  representing the preparation of the particle in the state described by  $|A\rangle$  is thus

$$\rho = |A\rangle\langle A| \quad (9)$$

The resolution of the identity

$$\mathbf{1} = \int |\mathbf{q}\rangle d^3q \langle \mathbf{q}| \quad (10)$$

permits us to write, with the help of Eq. (8),

$$|A\rangle = \int |\mathbf{q}\rangle d^3q \langle \mathbf{q} | A \rangle = \int |\mathbf{q}\rangle \psi(\mathbf{q}) d^3q \quad (11)$$

Writing Eq. (6) into Eq. (11) yields

$$|A\rangle = (2\pi/\Delta q^2)^{3/4} \{\exp[-(\mathbf{Q} - \langle \mathbf{q} | \mathbf{1} \rangle)^2/4\Delta q^2]\} |\langle \mathbf{p} \rangle\rangle \quad (12)$$

where  $\mathbf{Q}$  is the operator

$$\mathbf{Q} = \int |\mathbf{q}\rangle \mathbf{q} \langle \mathbf{q} | d^3q \quad (13)$$

and for any function (e.g., the exponential function)

$$f(\mathbf{Q}) = \int |\mathbf{q}\rangle f(\mathbf{q}) \langle \mathbf{q} | d^3q \quad (14)$$

The symbol  $|\langle \mathbf{p} \rangle\rangle$  in (12) denotes the Hilbert space vector associated with the mean momentum  $\langle \mathbf{p} \rangle$  such that

$$\langle \mathbf{q} | \langle \mathbf{p} \rangle\rangle = (2\pi)^{-3/2} \exp(i\mathbf{q} \cdot \langle \mathbf{p} \rangle) \quad (15)$$

When the system of interest consist of two particles, we need a Hilbert space for each,  $\mathcal{H}_A$  and  $\mathcal{H}_B$ , and the tensor product

$$\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B \quad (16)$$

becomes the appropriate space for the composite system. Let  $|A\rangle |B\rangle$  denote the abstract vector in  $\mathcal{H}$  represented by a pair of uncorrelated wave packets,  $|B\rangle$  being the exact analog of  $|A\rangle$  as written above in (12). The statistical operator in  $\mathcal{H}$  representing this pair of uncorrelated wave packets is the projector

$$\rho_{AB} = |A\rangle |B\rangle \langle B| \langle A| = \rho_A \otimes \rho_B \quad (17)$$

This preparation of the system may be chosen as a starting state at  $t = 0$ . Time evolution of the system will then proceed according to the quantum dynamical hypothesis:

$$\rho_{AB}(t) = e^{-itH} |A\rangle |B\rangle \langle B| \langle A| e^{itH} \quad (18)$$

where the Hamiltonian  $H$ , an operator in  $\mathcal{H}$ , has the form

$$H = H_A \times \mathbf{1}_B + \mathbf{1}_A \times H_B + V \quad (19)$$

where  $H_A$  operates only in  $\mathcal{H}_A$ ,  $H_B$  only in  $\mathcal{H}_B$ , but the interaction term  $V$  operates in  $\mathcal{H}$ . As is customary, the identities  $\mathbf{1}_A$ ,  $\mathbf{1}_B$  in  $\mathcal{H}_A$ ,  $\mathcal{H}_B$  will be

suppressed henceforth. Since the initial  $\rho$  is a projector and the dynamical evolution (18) is unitary, then  $\rho(t)$  is also pure. However, because of  $V$ ,  $\rho(t)$  can in general no longer be factored into separate statistical operators, one for each particle, because  $V$  couples  $\mathcal{H}_A$  and  $\mathcal{H}_B$ . Therefore a pair that has been prepared in two pure packets  $|A\rangle$  and  $|B\rangle$  does not in general remain separable into two packets during their evolution under the influence of the Hamiltonian.

Nevertheless, it is well known that when the interaction is a centrally symmetric potential, a function only of  $|\mathbf{Q}_A - \mathbf{Q}_B|$ , we can resort to the classical decoupling procedure, the transformation to relative and center-of-mass coordinates in which the Hamiltonian becomes

$$H = H_A + H_B + V = H_C + H_R \quad (20)$$

where  $H_C$  depends only on the center-of-mass momentum, and  $H_R$  only on the relative coordinates and momenta. Using this, we form a refactoring of the Hilbert space

$$\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B = \mathcal{H}_C \otimes \mathcal{H}_R \quad (21)$$

where the operators  $H_C$  and  $H_R$  perform, only in the spaces  $\mathcal{H}_C$  and  $\mathcal{H}_R$ . As classically, we now have two quasiparticles,  $C$  and  $R$ , with effective masses and motions that differ from those of the physical particles we started with.

We shall demonstrate below that, under a certain rather special condition, the two minimum uncertainty wave packets  $|A\rangle$  and  $|B\rangle$  transform into two uncorrelated quasiparticle minimum-uncertainty wave packets  $|C\rangle$  and  $|R\rangle$  in the new spaces  $\mathcal{H}_C$  and  $\mathcal{H}_R$  and that they then evolve under the influence of their respective Hamiltonians independently and remain uncorrelated. To be more explicit, when this special condition is satisfied, then

$$|A\rangle |B\rangle = |C\rangle |R\rangle \quad (22)$$

and the statistical operator (18) can also be written

$$\rho_{AB}(t) = \rho_{CR}(t) = e^{-itH} |C\rangle |R\rangle \langle R| \langle C| e^{itH} \quad (23)$$

Hence, using (20) and remembering that because  $H_C$  and  $H_R$  operate in separate spaces they commute, we can rearrange the factors in (23) as follows:

$$\rho_{CR}(t) = e^{-itH_C} |C\rangle \langle C| e^{itH_C} \otimes e^{-itH_R} |R\rangle \langle R| e^{itH_R} \quad (24)$$

The statistical operator is thus factorizable at all times,

$$\rho_{CR}(t) = \rho_C(t) \otimes \rho_R(t) \quad (25)$$

and in this case motions of the quasiparticles can be determined independently; and a reverse transformation back to actual particles can give us the complete solution for  $\rho(t)$ .

Unfortunately, even though the decoupling indicated by (20) and (21) is always possible for centrally symmetric interactions, the *factorization* (22) is usually impossible; and we shall have to reconsider the dynamical problem more carefully after studying the general form of  $\rho(t)$  in the next sections.

### 3. TRANSFORMATION TO RELATIVE COORDINATES

Let the particles have masses  $M_A$  and  $M_B$ , with  $M_B > M_A$ , and define the quasiparticle masses:

$$M = M_A + M_B, \quad \mu = M_A M_B / M \tag{26}$$

Writing

$$M_A/M = \alpha, \quad M_B/M = 1 - \alpha, \quad \alpha \equiv \frac{1}{2}[1 - (1 - 4\mu/M)^{1/2}] \tag{27}$$

we may then express the familiar classical coordinate transformation between  $\mathbf{q}_A, \mathbf{q}_B$  and  $\mathbf{q}_R, \mathbf{q}_C$  as

$$\left\{ \begin{matrix} \mathbf{q}_R = \mathbf{q}_A - \mathbf{q}_B \\ \mathbf{q}_C = \alpha \mathbf{q}_A = (1 - \alpha) \mathbf{q}_B \end{matrix} \right\} \leftrightarrow \left\{ \begin{matrix} \mathbf{q}_A = \mathbf{q}_C + (1 - \alpha) \mathbf{q}_R \\ \mathbf{q}_B = \mathbf{q}_C - \alpha \mathbf{q}_R \end{matrix} \right\} \tag{28}$$

with the corresponding momentum transformation given by

$$\left\{ \begin{matrix} \mathbf{p}_R = (1 - \alpha) \mathbf{p}_A - \alpha \mathbf{p}_B \\ \mathbf{p}_C = \mathbf{p}_A + \mathbf{p}_B \end{matrix} \right\} \leftrightarrow \left\{ \begin{matrix} \mathbf{p}_A = \alpha \mathbf{p}_C + \mathbf{p}_R \\ \mathbf{p}_B = (1 - \alpha) \mathbf{p}_C - \mathbf{p}_R \end{matrix} \right\} \tag{29}$$

From these it follows that

$$\mathbf{p}_C = M \dot{\mathbf{q}}_C, \quad \mathbf{p}_R = \mu \dot{\mathbf{q}}_R, \quad p_A^2/2M_A + p_B^2/2M_B = p_C^2/2M + p_R^2/2\mu \tag{30}$$

All of these equations are immediately valid also for the corresponding quantum mechanical operators and their mean values  $\langle \mathbf{q}_A \rangle, \langle \mathbf{q}_B \rangle, \langle \mathbf{q}_R \rangle, \langle \mathbf{q}_C \rangle, \langle \mathbf{p}_A \rangle$ , etc.

To study quantum states under the transformation from  $AB$  to  $CR$ , we need the following delta function analogs of the classical transformations. Corresponding to (28) we write

$$\begin{aligned} \langle \mathbf{q}_A | \langle \mathbf{q}_B | | \mathbf{q}_C \rangle | \mathbf{q}_R \rangle &= \delta(\mathbf{q}_R - [\mathbf{q}_A - \mathbf{q}_B]) \delta(\mathbf{q}_C - [\alpha \mathbf{q}_A + (1 - \alpha) \mathbf{q}_B]) \\ &= \delta(\mathbf{q}_A - [\mathbf{q}_C + (1 - \alpha) \mathbf{q}_R]) \delta(\mathbf{q}_B - [\mathbf{q}_C - \alpha \mathbf{q}_R]) \end{aligned} \tag{31}$$

and corresponding to (29) we write

$$\begin{aligned} \langle \mathbf{p}_A | \langle \mathbf{p}_B | | \mathbf{p}_C \rangle | \mathbf{p}_R \rangle &= \delta(\mathbf{p}_R - [(1 - \alpha) \mathbf{p}_A - \alpha \mathbf{p}_B]) \delta(\mathbf{p}_C - [\mathbf{p}_A + \mathbf{p}_B]) \\ &= \delta(\mathbf{p}_A - [\alpha \mathbf{p}_C + \mathbf{p}_R]) \delta(\mathbf{p}_B - [(1 - \alpha) \mathbf{p}_C - \mathbf{p}_R]) \end{aligned} \quad (32)$$

We are now in a position to transform the wave packet  $|A\rangle |B\rangle$  into the new coordinates and momenta of the quasiparticles. To do, this we can operate on  $|A\rangle |B\rangle$  with the identity in  $\mathcal{H}$  to obtain

$$|A\rangle |B\rangle = \int d^3q_C d^3q_R | \mathbf{q}_C \rangle | \mathbf{q}_R \rangle \langle \mathbf{q}_C | |A\rangle |B\rangle \quad (33)$$

and then use the form (12) for each of the original packets, which yields

$$\begin{aligned} |A\rangle |B\rangle &= (2\pi)^3 (2\pi \Delta q_A^2)^{-3/4} (2\pi \Delta q_B^2)^{-3/4} \int d^3q_C \int d^3q_R | \mathbf{q}_C \rangle | \mathbf{q}_R \rangle \\ &\quad \times \{ \langle \mathbf{q}_R | \langle \mathbf{q}_C | \exp[-(\mathbf{Q}_A - \langle \mathbf{q}_A \rangle)^2 / 4\Delta q_A^2] | \langle \mathbf{p}_A \rangle \rangle \\ &\quad \times \exp[-(\mathbf{Q}_B - \langle \mathbf{q}_B \rangle)^2 / 4\Delta q_B^2] | \langle \mathbf{p}_B \rangle \rangle \} \end{aligned} \quad (34)$$

When the operators are written out in full, the quantity in curly brackets in (34) becomes

$$\begin{aligned} &\int d^3q_A \int d^3q_B \langle \mathbf{q}_R | \langle \mathbf{q}_C | | \mathbf{q}_A \rangle | \mathbf{q}_B \rangle (2\pi)^{-3} \\ &\quad \times \exp\{i[\mathbf{q}_A \cdot \langle \mathbf{p}_A \rangle + \mathbf{q}_B \cdot \langle \mathbf{p}_B \rangle]\} \\ &\quad \times \exp[-(\mathbf{q}_A - \langle \mathbf{q}_A \rangle)^2 / 4\Delta q_A^2 - (\mathbf{q}_B - \langle \mathbf{q}_B \rangle)^2 / 4\Delta q_B^2] \end{aligned} \quad (35)$$

Performing the integration using the second form of (31) and the classical transformations for the averages  $\langle q_A \rangle$ ,  $\langle q_B \rangle$ , etc., we reduce the expression in (35) as follows:

$$\begin{aligned} &(2\pi)^{-3} \exp\{i[\mathbf{q}_C + (1 - \alpha) \mathbf{q}_R] \cdot (\alpha \langle \mathbf{p}_C \rangle + \langle \mathbf{p}_R \rangle) \\ &\quad + i(\mathbf{q}_C - \alpha \mathbf{q}_R) \cdot [(1 - \alpha) \langle \mathbf{p}_C \rangle - \langle \mathbf{p}_R \rangle] \\ &\quad - (\mathbf{q}_C - \langle \mathbf{q}_C \rangle)^2 [1/(4\Delta q_A^2) + 1/(4\Delta q_B^2)] \\ &\quad - (\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 [(1 - \alpha)^2 / (4\Delta q_A^2) + \alpha^2 / (4\Delta q_B^2)] \\ &\quad - 2(\mathbf{q}_C - \langle \mathbf{q}_C \rangle) \cdot (\mathbf{q}_R - \langle \mathbf{q}_R \rangle) [(1 - \alpha) / (4\Delta q_A^2) - \alpha / (4\Delta q_B^2)] \} \end{aligned}$$

Upon rearrangement of the exponents, this becomes

$$\begin{aligned} &(2\pi)^{-3} \exp\{i\mathbf{q}_C \cdot \langle \mathbf{p}_C \rangle - (\mathbf{q}_C - \langle \mathbf{q}_C \rangle)^2 [1/(4\Delta q_A^2) + 1/(4\Delta q_B^2)]\} \\ &\quad \times \exp\{i\mathbf{q}_R \cdot \langle \mathbf{p}_R \rangle - (\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 [(1 - \alpha)^2 / (4\Delta q_A^2) + \alpha^2 / (4\Delta q_B^2)]\} \\ &\quad \times \exp\{-2(\mathbf{q}_C - \langle \mathbf{q}_C \rangle) \cdot (\mathbf{q}_R - \langle \mathbf{q}_R \rangle) [(1 + \alpha) / (4\Delta q_A^2) - \alpha / (4\Delta q_B^2)]\} \end{aligned} \quad (36)$$

Substituting (36) into (34), we obtain finally

$$\begin{aligned}
 |A\rangle |B\rangle &= (2\pi \Delta q_A^2)^{-3/4} (2\pi \Delta q_B^2)^{-3/4} \int d^3 q_C \int d^3 q_R |q_C\rangle |q_R\rangle \\
 &\quad \times \exp(iq_C \cdot \langle p_C \rangle) \exp[-(\mathbf{q}_C - \langle \mathbf{q}_C \rangle)^2 / (4\Delta q_C^2)] \\
 &\quad \times \exp(iq_R \cdot \langle p_R \rangle) \exp[-(\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 / (4\Delta q_R^2)] \\
 &\quad \times \exp[-2(\mathbf{q}_C - \langle \mathbf{q}_C \rangle) \cdot (\mathbf{q}_R - \langle \mathbf{q}_R \rangle) \gamma]
 \end{aligned} \tag{37}$$

where

$$\gamma \equiv (1 - \alpha) / (4\Delta q_A^2) - \alpha / (4\Delta q_B^2) \tag{38}$$

and

$$1/\Delta q_C^2 = 1/\Delta q_A^2 + 1/\Delta q_B^2, \quad 1/\Delta q_R^2 = (1 - \alpha)^2/\Delta q_A^2 + \alpha^2/\Delta q_B^2 \tag{39}$$

#### 4. DISPERSION MATCHING CONDITION

It seems clear from (37) that  $|A\rangle |B\rangle$  can factorize into the form  $|C\rangle |R\rangle$  if and only if the last exponent in (37) varies with neither  $\mathbf{q}_R$  nor  $\mathbf{q}_C$ . Thus the necessary and sufficient condition for this separability would be

$$(1 - \alpha) / (4\Delta q_A^2) = \alpha / (4\Delta q_B^2) \tag{40}$$

which becomes, after insertion of the definition of  $\alpha$  from (27), the simple expression

$$M_A \Delta q_A^2 = M_B \Delta q_B^2 \tag{41}$$

which, incidentally, when combined with (39) yields

$$\Delta q_C^2 \Delta q_R^2 = \Delta q_A^2 \Delta q_B^2 \tag{42}$$

If (42), which we shall call the *dispersion matching condition*, is satisfied, (37) assumes the form

$$\begin{aligned}
 |A\rangle |B\rangle &= (2\pi \Delta q_A^2)^{-3/4} (2\pi \Delta q_B^2)^{-3/4} \\
 &\quad \times \int d^3 q_C |q_C\rangle \exp\{iq_C \cdot \langle p_C \rangle - (\mathbf{q}_C - \langle \mathbf{q}_C \rangle)^2 \\
 &\quad \times [1/(4\Delta q_A^2) + 1/(4\Delta q_B^2)]\} \\
 &\quad \times \int d^3 q_R |q_R\rangle \exp\{iq_R \cdot \langle p_R \rangle - (\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 \\
 &\quad \times [(1 - \alpha)^2/(4\Delta q_A^2) + \alpha^2/(4\Delta q_B^2)]\}
 \end{aligned} \tag{43}$$



and therefore we have, as contemplated in (22),

$$|A\rangle |B\rangle = |C\rangle |R\rangle \tag{44}$$

where

$$\begin{aligned} |C\rangle &= (2\pi)^{3/2} (2\pi \Delta q_C^2)^{-3/4} \exp[-(\mathbf{Q}_C - \langle \mathbf{q}_C \rangle \mathbf{1}_C)^2 / 4\Delta q_C^2] |\langle \mathbf{p}_C \rangle\rangle \\ |R\rangle &= (2\pi)^{3/2} (2\pi \Delta q_R^2)^{-3/4} \exp[-(\mathbf{Q}_R - \langle \mathbf{q}_R \rangle \mathbf{1}_R)^2 / 4\Delta q_R^2] |\langle \mathbf{p}_R \rangle\rangle \end{aligned} \tag{45}$$

The expressions in (45) are precise analogs of the expression for  $|A\rangle$  in (12), and represent minimum uncertainty wave packets of the two quasiparticles, which will evolve independently of each other. Again we stress, however, that this result is not a general theorem, but has been derived only under the proviso that the dispersion matching condition (42) is satisfied.

To establish beyond doubt that the dispersion matching condition is necessary and sufficient for the state factorization (44), we next extract from the statistical operator

$$\rho_{AB} = |A\rangle |B\rangle \langle B| \langle A| = \rho_{CR} \tag{46}$$

the reduced statistical operator  $\rho_R$  for the  $R$  quasiparticle alone in the general case where the dispersion matching condition is not assumed. Substitution of (37) into (5) yields

$$\rho_R = \text{Tr}_C \rho_{CR} = \int d^3q_C' \langle \mathbf{q}_C' | \rho | \mathbf{q}_C' \rangle \tag{47}$$

$$= (2\pi \Delta q_A^2)^{-3/2} (2\pi \Delta q_B^2)^{-3/2} \int d^3q_R \int d^3q_R' | \mathbf{q}_R \rangle I(R, R') \langle \mathbf{q}_R' | \tag{48}$$

where

$$\begin{aligned} I(R, R') &= \int d^3q_C \{ \exp[-(\mathbf{q}_C - \langle \mathbf{q}_C \rangle)^2 / (2\Delta q_C^2)] \\ &\quad \times \exp\{-2(\mathbf{q}_C - \langle \mathbf{q}_C \rangle) \cdot \{(\mathbf{q}_R - \langle \mathbf{q}_R \rangle) + (q_R' - \langle \mathbf{q}_R \rangle)\} \gamma\} \\ &\quad \times \exp[-(\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 / (4\Delta q_R^2)] \\ &\quad \times \exp[-(\mathbf{q}_R' - \langle \mathbf{q}_R \rangle)^2 / (4\Delta q_R^2)] \exp[i\langle \mathbf{p}_R \rangle \cdot (\mathbf{q}_R - \mathbf{q}_R')] \} \\ &= \int d^3q_C \exp\{-[1/2\Delta q_C^2][(\mathbf{q}_C - \langle \mathbf{q}_C \rangle) \\ &\quad + (\mathbf{q}_R - \langle \mathbf{q}_R \rangle + \mathbf{q}_R' - \langle \mathbf{q}_R \rangle) 2\Delta q_C^2 \gamma]^2\} \\ &\quad \times \exp[(\mathbf{q}_R - \langle \mathbf{q}_R \rangle + \mathbf{q}_R' - \langle \mathbf{q}_R \rangle)^2 2\Delta q_C^2 \gamma^2] \\ &\quad \times \exp[-(\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 / (4\Delta q_R^2)] \exp[-(\mathbf{q}_R' - \langle \mathbf{q}_R \rangle)^2 / (4\Delta q_R^2)] \\ &\quad \times \exp[i\langle \mathbf{p} \rangle \cdot (\mathbf{q}_R - \mathbf{q}_R')] \} \end{aligned} \tag{49}$$

The integral is elementary and we have

$$\begin{aligned}
 I(R, R') &= (2\pi \Delta q_C^2)^{3/2} \\
 &\times \exp\{-[(\mathbf{q}_R - \langle \mathbf{q}_R \rangle)^2 + (\mathbf{q}_{R'} - \langle \mathbf{q}_R \rangle)^2][1/(4\Delta q_R^2) - 2\Delta q_C^2 \gamma^2]\} \\
 &\times \exp[4\Delta q_C^2 \gamma^2 (\mathbf{q}_R - \langle \mathbf{q}_R \rangle) \cdot (\mathbf{q}_{R'} - \langle \mathbf{q}_R \rangle)] \\
 &\times \exp[i\langle \mathbf{p}_R \rangle \cdot (\mathbf{q}_R - \mathbf{q}_{R'})] \quad (51)
 \end{aligned}$$

To determine if the  $R$  quasiparticle is in a pure or mixed quantum state, we consider

$$\begin{aligned}
 \text{Tr } \rho_R^2 &= (2\pi \Delta q_A^2)^{-3} (2\pi \Delta q_B^2)^{-3} (2\pi \Delta q_C^2)^3 \\
 &\times \int d^3 q_R \int d^3 q_{R'} I(R, R') I(R', R) \quad (52)
 \end{aligned}$$

The integrals are easily evaluated to obtain

$$\begin{aligned}
 \text{Tr } \rho_R^2 &= (\Delta q_R^2 \Delta q_C^2 / \Delta q_A^2 \Delta q_B^2)^3 \\
 &\times [(1 - 8\Delta q_R^2 \Delta q_C^2 \gamma^2)^2 + 8\Delta q_R^2 \Delta q_C^2 \gamma^2]^{-3/2} \quad (53)
 \end{aligned}$$

Using the relations in (38) and (39), this can be reduced to

$$\text{Tr } \rho_R^2 = (1 - B^2)^3 [(1 - \frac{1}{2}B^2)^2 + \frac{1}{2}B^2]^{-3/2} \quad (54)$$

where

$$B^2 \equiv \frac{[(1 - \alpha) \Delta q_B^2 - \alpha \Delta q_A^2]^2}{\Delta q_A^2 \Delta q_B^2 + [(1 - \alpha) \Delta q_B^2 - \alpha \Delta q_A^2]^2} \quad (55)$$

It is a well-known theorem that a density operator  $\rho_R$  is pure if and only if

$$\text{Tr } \rho_R^2 = 1 \quad (56)$$

Substituting (54) into (56), we find that  $B^2 = 0$  is the only real, nonnegative root of the resulting equation in  $B^2$ . Setting  $B^2 = 0$  in (55) leads again to the dispersion matching condition (42), which appears here as the necessary and sufficient condition for  $\rho_R$  to be pure.

According to a theorem due to von Neumann,<sup>(2)</sup> if  $\rho_R$  is pure, then the total state  $\rho_{AB} = \rho_{CR}$  will be given by  $\rho_C \otimes \rho_R$ , where  $\rho_C$  is the reduced statistical operator for the  $C$  quasiparticle; i.e.,

$$\rho_{AB} = |A\rangle |B\rangle \langle B| \langle A| = \rho_C \otimes \rho_R = \rho_{CR} \quad (57)$$

Thus, since  $\rho_{CR} = \rho_{AB}$  is pure, it follows that either both  $\rho_R$  and  $\rho_C$  are pure or else both are mixed. The dispersion matching condition for the purity of  $\rho_R$  is therefore also the necessary and sufficient condition for the factorization (44), as expected.

If  $\alpha \rightarrow 0$  ( $M_B/M_A \rightarrow 0$ ) and  $\Delta q_B^2 \rightarrow 0$ , then  $B^2 \rightarrow 0$ , whatever one may choose for  $\Delta q_A^2$ . This corresponds to the fact that scattering by a fixed force center cannot cause a pure state to become mixed. However, if the two masses are comparable,  $\alpha$  not near zero, there is no way to make  $B^2$  approach zero except by satisfying the dispersion matching condition (41). If we prepare both particles in nearly pure momentum states  $\Delta p_A$  and  $\Delta p_B$  both small, we may use the relation  $\Delta p_A \Delta q_A = \Delta p_B \Delta q_B = \frac{1}{2}$  to convert (55) into

$$B^2 = X^2/(1 + X^2), \quad X = (1 - \alpha) \Delta p_A/\Delta p_B - \alpha \Delta p_B/\Delta p_A \quad (58)$$

and again there is no way to make this vanish except by satisfying the same dispersion matching condition (41) in the form

$$(1 - \alpha)/\Delta p_B^2 = \alpha/\Delta p_A^2 \quad (59)$$

On the other hand, with heavy targets the situation is better. One might prepare the projectile  $A$  with sharp momentum ( $\Delta p_A$  small) and the target with sharp location ( $\Delta q_B$  small). To make estimates we go over from natural to cgs units so that  $\hbar$  appears explicitly ( $\Delta p_A \Delta q_A = \Delta p_B \Delta q_B = \frac{1}{2}\hbar$ ) and write in place of (55) the equation

$$B^2 = Y^2/(4\Delta q_B^2 \Delta p_A^2/\hbar^2 + Y^2) \quad (60)$$

where

$$Y \equiv (1 - \alpha) 4\Delta q_B^2 \Delta p_A^2/\hbar^2 - \alpha$$

Consider a neutron, mass  $\sim 10^{-24}$  g, with a speed  $\sim 10^5$  cm/sec; we would consider the momentum sharp if  $\Delta p_A \approx 10^{-21}$  g cm/sec. If the target were a nucleus of atomic mass  $\sim 100$ , so that  $\alpha = 0.01$ , then purity of the  $R$  particle demands  $4\Delta q_B^2 \times 10^{-42} \approx 0.01 \times 4 \times 10^{-53}$ , or  $\Delta q_B^2 \approx 10^{-13}$ , which is a realistic enough result. Similarly, an electron projectile and proton target with  $\Delta p_A \approx 10^{-24}$  would demand  $\Delta q_B^2 \approx 10^{-14}$  for approximate purity of  $\rho_R$ . Evidently it is only for particles of similar mass that the dispersion matching restriction could have any noticeable impact on the conventional scattering theory, which routinely assumes that  $\rho_R$  is pure. Finally we note that from Eq. (55)

$$B^2 = \frac{[(1 - \alpha)\mu - \alpha]^2}{\mu + [(1 - \alpha)\mu - \alpha]^2} \quad \text{where} \quad \mu = \frac{\Delta q_B^2}{\Delta q_A^2} = \frac{\Delta p_A^2}{\Delta p_B^2} \quad (61)$$

and alternatively, provided  $\alpha \neq \frac{1}{2}$ ,

$$B^2 = \frac{[1 - \alpha\beta(1 - \alpha)]^2}{\beta(1 - 2\alpha)^2} \quad \text{where} \quad \frac{1}{\beta} = \frac{\Delta q_C^2}{\Delta q_R^2} = \frac{\Delta p_R^2}{\Delta p_C^2} \quad (62)$$

{Note  $\mu = (\alpha^2\beta - 1)/[1 - (1 - \alpha)^2\beta]$ .}

From these expressions it is clear that the dispersion matching values are

$$\mu_m = \alpha/(1 - \alpha) \quad \text{and} \quad \beta_m = 1/\alpha(1 - \alpha)$$

If one maintains a given ratio  $\mu$  or  $\beta$ , different from  $\mu_m$  or  $\beta_m$ , then  $B^2$  remains nonzero even when  $\Delta p_A^2 \rightarrow 0$ , and  $\Delta p_B^2 \rightarrow 0$ . Thus, incident particles in pure wave packet states that are almost pure momentum states map into quasiparticles that are not pure states, even though their respective dispersions  $\Delta p_C^2$  and  $\Delta p_R^2$  approach zero. For example, with a heavy target,  $\alpha \rightarrow 0$ , we have  $B^2 \rightarrow \mu/(1 + \mu) = 1/\beta$  and to achieve purity in  $\rho_R$  we must be sure the center of mass of the system is much more precisely located than either of the two particles, so that  $\Delta q_C^2 \ll \Delta q_R^2$ ,  $1/\beta \rightarrow 0$ .

This point is a good illustration of the inadequacy of the "ignorance interpretation" of the density matrix, which regards the latter as a technique for handling the "odds" on the true pure state when that is not known. Here we have two particles  $A, B$  prepared in precisely known pure states (wave packets) and yet in the  $CR$  representation the perfectly well-defined quasiparticles turn out to have mixed states when their dispersions are not matched. On the ignorance interpretation of the density matrix this would be understood to assert that a known transformation has produced unknown states from known states! In our work we maintain that the true state is described at all times by the density matrix; there is no ignorance involved in the mixed cases.

## 5. DYNAMICAL CONSIDERATIONS

The  $S$ -matrix formalism leads to considerable clarification of these questions. It is usually presented<sup>(3)</sup> as a powerful technique for calculating cross sections for particles prepared in pure states, while the density matrix is usually introduced for mixed states with the ignorance interpretation. Here we outline very briefly how the formalism should be handled from the newer point of view, using the statistical operator as the state, whether represented by a pure or a mixed density matrix, evolving in time through collision processes.

We have quite generally (Ref. 3, Chapter 3 and §4.6)

$$\rho_{\text{out}} = S \rho_{\text{in}} S^\dagger \quad (63)$$

where

$$S \equiv [\text{Lim}_{t \rightarrow \infty} \exp(-iHt) \exp(iH^0t)] [\text{Lim}_{t \rightarrow -\infty} \exp(iHt) \exp(-iH^0t)] \quad (64)$$

Here  $H$  is the total Hamiltonian, while  $H^0$  is the kinetic energy part of the Hamiltonian. Going over to the quasiparticle  $CR$  representation, we have

$$H = 1_R \otimes H_C + H_R \otimes 1_C, \quad H^0 = 1_R \otimes H_C^0 + H_R^0 \otimes 1_C \quad (65)$$

The two parts of  $H$  and the two parts of  $H^0$  commute, so we have

$$S = 1_C \otimes S_R \tag{66}$$

where

$$S_R = [\text{Lim}_{t \rightarrow \infty} \exp(-iH_R t) \exp(iH_R^0 t)] [\text{Lim}_{t \rightarrow -\infty} \exp(iH_R t) \exp(-iH_R^0 t)]$$

We may now write Eq. (63) as

$$\rho_{out} = S_R \rho_{in} S_R^\dagger \tag{67}$$

and adapt the formalism to collision situations by writing

$$S_R = 1_R + iK \tag{68}$$

as the definition of  $K$ , the part of  $S$  that is effectively the scattering operator. Then we have from (67)

$$\rho_{out} = \rho_{in} + iK\rho_{in} - i\rho_{in}K^\dagger + K\rho_{in}K^\dagger \tag{69}$$

At this point we have a choice, either the  $AB$  or the  $CR$  representation for  $\rho$ . Since  $K$  operates only in  $\mathcal{H}_R$ , the simplest procedure is usually to write  $\rho_{CR}$  for the state  $\rho$ , and to define the state of the quasiparticle  $R$  as

$$\rho_R = \text{Tr}_C \rho_{CR} \tag{70}$$

Then Eq. (69) becomes

$$\rho_{R,out} = \rho_{R,in} + iK\rho_{R,in} - i\rho_{R,in}K^\dagger + K\rho_{R,in}K^\dagger \tag{71}$$

If  $\rho_{R,in}$  is a pure momentum state, we may write

$$\rho_{R,in} = |p^0\rangle\langle p^0| \tag{72}$$

and the probability of finding the momentum  $p$  in  $\rho_{R,out}$  is

$$\begin{aligned} \langle p | \rho_{R,out} | p \rangle &= \delta(p - p^0) \delta(p - p^0) + i\langle p | K | p^0 \rangle \delta(p - p^0) \\ &\quad - i\delta(p - p^0) \langle p^0 | K^\dagger | p \rangle + |\langle p | K | p^0 \rangle|^2 \end{aligned} \tag{73}$$

To “remove the unscattered wave” we assume that  $p \neq p^0$ , and so derive the standard result

$$\langle p | \rho_{R,out} | p \rangle = |\langle p | K | p^0 \rangle|^2 = \delta(E_p - E_{p^0}) d\sigma/d\Omega \tag{74}$$

Essentially we may regard this as the formal definition of the cross section.

As a second example, let  $\rho_{R,in}$  be a mixture of momentum states:

$$\rho_{R,in} = \sum_k w_k |p_k\rangle\langle p_k| \tag{75}$$

and again assume that none of the incident unscattered momenta are to be observed; then from (71) and (75) we find

$$\langle p | \rho_{R,\text{out}} | p \rangle = \sum_k w_k |\langle p | K | p_k \rangle|^2 \quad (76)$$

which permits the standard interpretation of the total cross section as a weighted average of the cross sections for the components of the mixture—incidentally, the same result as would be obtained from the ignorance interpretation of the density matrix.

As a third example let  $\rho_{R,\text{in}}$  be a pure state wave packet as in Eq. (46):

$$\rho_{R,\text{in}} = |R\rangle\langle R| \quad (77)$$

and assume the wave packet sharp enough to be able to remove the unscattered wave from observation:

$$\langle p | R \rangle = 0 \quad (78)$$

Then, applying Eqs. (77) and (78) to (71), we have

$$\langle p | \rho_{R,\text{out}} | p \rangle = \langle p | K | R \rangle \langle R | K | p \rangle = \left| \int dp' \langle p | K | p' \rangle \langle p' | R \rangle \right|^2 \quad (79)$$

Here the factor  $\langle p' | R \rangle$  is the amplitude of the momentum  $p'$  component in the wave packet  $|R\rangle$ , the integral is inside the square modulus, and the cross section  $|\langle p | K | p' \rangle|^2$  does not occur in the expression for  $\langle p | \rho_{R,\text{out}} | p \rangle$ . Only insofar as  $\langle p' | R \rangle$  is very sharply peaked about, say,  $p_0$  does Eq. (79) reduce approximately to the cross-section expression  $|\langle p | K | p_0 \rangle \langle p_0 | R \rangle|^2$ .

Now consider the case where the  $A$  and  $B$  wave packets were not matched, so that  $\rho_{CR}$  does not factorize into separate operators. In this case we can use neither the form (75) nor (77), and must use the more general expression

$$\rho_{R,\text{in}} = \int dp' \int dp'' |p'\rangle G(p', p'') \langle p''| \quad (80)$$

where  $G(p', p'')$  is a function of the two momenta, which cannot be factorized into separate functions—e.g., Eqs. (48) and (51). Again assuming that  $\rho_{R,\text{in}}$  is a realistic state prepared for a collision,

$$\rho_{R,\text{in}} |p\rangle = 0 \quad (81)$$

Eq. (71) yields

$$\langle p | \rho_{R,\text{out}} | p \rangle = \int dp' \int dp'' \langle p | K | p' \rangle G(p', p'') \langle p'' | K | p \rangle \quad (82)$$

In principle  $G(p', p'')$  could be diagonalized in some representation other than momentum, say

$$\rho_{R,\text{in}} = \int dn |n\rangle G_n \langle n| \quad (83)$$

and

$$\langle p | \rho_{R,\text{out}} | p \rangle = \int dn G_n |\langle p | K | n \rangle|^2 \quad (84)$$

But  $|n\rangle$  is not a momentum vector, so  $|\langle p | K | n \rangle|^2$  is not a cross section. More precisely we should write

$$\langle p | \rho_{R,\text{out}} | p \rangle = \int dn G_n \left| \int dp' \langle p | K | p' \rangle \langle p' | n \rangle \right|^2 \quad (85)$$

which, like Eq. (79), does not allow the use of the cross section.

A familiar strategy in the case where  $\rho_{R,\text{in}}$  is a mixture that is not diagonal in the  $p$  representation is to remain in the  $AB$  representation for  $\rho$ . But because  $K$  operates partly in the  $A$  space and partly in the  $B$  space, we must go back to Eq. (69), assume that  $\rho$  is a pure state of the form (46),

$$\rho_{\text{in}} = |A\rangle |B\rangle \langle B| \langle A|$$

and assume that the incoming packets are well enough defined to allow removal of the unscattered waves:

$$\langle p_A | A \rangle = \langle p_B | B \rangle = 0 \quad (86)$$

so that we have from Eq. (69)

$$\begin{aligned} & \langle p_A | \langle p_B | \rho_{\text{out}} | p_B \rangle | p_A \rangle \\ &= \langle p_A | \langle p_B | K | B \rangle | A \rangle \langle A | \langle B | K | p_B \rangle | p_A \rangle \\ &= \left| \int dp_A' \int dp_B' \langle p_A | \langle p_B | K | p_B' \rangle | p_A' \rangle \langle p_A' | \langle p_B' | B \rangle | A \rangle \right|^2 \quad (87) \end{aligned}$$

Just like Eq. (79), this does not involve the cross section unless the wave packets are exceedingly sharp, and this method does not really solve the problem posed by Eqs. (80)–(85). From all these examples it is clear that except in very restricted circumstances, the essential parameter is the complex scattering amplitude, not the cross section, when collision theory is extended beyond pure momentum eigenstates. One cannot use the cross section to predict the outcome of collisions in any other situations than those specially prepared for the measurement of the cross section!

## 6. DISCUSSION

One conclusion is clear: there is much more implied by the  $AB \leftrightarrow CR$  transformation in quantum theory than there was in classical mechanics. In the familiar classical theory one regarded the  $R$  quasiparticle simply as what an observer would see of the  $A$  particle if he took up residence on the  $B$  particle; or, in the jargon that is often used also in quantum theory,  $R$  is what  $A$  “looks like” to  $B$ . In quantum theory a change in “point of view” or frame of reference is described by an unitary transformation; but such a transformation cannot change  $\rho_A$  to  $\rho_R$  because, as we have seen, while  $\rho_A$  may be pure ( $\text{Tr } \rho_A^2 = 1$ ), in general  $\rho_R$  will then not be pure ( $\text{Tr } \rho_R^2 < 1$ ). But the trace is invariant under any unitary transformation, so in quantum mechanics we cannot consistently interpret the  $R$  quasiparticle to be the  $A$  particle as “seen by” the  $B$  particle.

In adapting the  $CR$  picture to the quantum mechanical problem we are obliged to realize that the  $R$  quasiparticle is not an aspect of the  $A$  particle, but a fictitious composite of both  $A$  and  $B$  invented solely for computational convenience in a specific problem. The use of the  $CR$  picture for any other purpose can lead to quite erroneous results, and the classical interpretation, while temptingly simple, is most deceptive.

The general results of Section 5 are important for the kinetic theory of gases. Classically, it is assumed that the cross-section theory of scattering is adequate for the discussion of such phenomena as diffusion and viscosity, etc., where the physical picture has always been based on the concept of a mean free path between successive pair collisions. But here we have found reason to doubt the basic validity of this assumption. Any particle emerging from one collision, even if that first collision were prearranged to satisfy the validity conditions, cannot possibly be in a state that would validate the cross-section theory of any subsequent collision with another particle. To see this quite clearly, we may imagine two particles  $A$  and  $B_1$  prepared in dispersion matched pure wave packets and write

$$\rho_{in,1} = |A\rangle |B_1\rangle \langle B_1| \langle A| = |R_1\rangle |C_1\rangle \langle C_1| \langle R_1| \quad (88)$$

They undergo a collision and emerge in the state

$$\rho_{out,1} = |R_{1,out}\rangle |C_1\rangle \langle C_1| \langle R_{1,out}| \quad (89)$$

The emerging state of  $A$  is then

$$\rho_{A,out,1} = \text{Tr}_{B_1}(|R_{1,out}\rangle |C_1\rangle \langle C_1| \langle R_{1,out}|) \quad (90)$$



whose matrix elements are

$$\begin{aligned}
 \langle p_A | \rho_{A,\text{out},1} | p_A' \rangle &= \langle p_A | \int dp_B \langle p_B | R_{1,\text{out}} \rangle | C_1 \rangle \langle C_1 | \langle R_{1,\text{out}} | p_B \rangle | p_A' \rangle \\
 &= \int dp_B \int dp_R \int dp_R' \int dp_C \int dp_C' \\
 &\quad \times \langle p_A | \langle p_B | p_R \rangle | p_C \rangle \langle p_C' | \langle p_R' | p_B \rangle | p_A' \rangle \\
 &\quad \times \langle p_R | R_{1,\text{out}} \rangle \langle R_{1,\text{out}} | p_R' \rangle \langle p_C | C_1 \rangle \langle C_1 | p_C' \rangle \quad (91)
 \end{aligned}$$

Assuming [cf. Eq. (45)] that  $\langle p_R | R \rangle$  and  $\langle p_C | C_1 \rangle$  have the factors  $\exp(-p_R^2/4\Delta p_R^2)$  and  $\exp(-p_C^2/4\Delta p_C^2)$ , and using the transformers of Eq. (32), we see that the matrix element of Eq. (92) has the factors

$$\begin{aligned}
 &\int dp_B \exp\{-[(1-\alpha)p_A - \alpha p_B]^2/(4\Delta p_R^2)\} \\
 &\quad \times \exp[-(p_A + p_B)^2/(4\Delta p_C^2)] \exp\{-[(1-\alpha)p_A' - \alpha p_B]^2/(4\Delta p_R^2)\} \\
 &\quad \times \exp[-(p_A' + p_B)^2/(4\Delta p_C^2)] \quad (92)
 \end{aligned}$$

Thus the outgoing state of the scattered particle is neither pure nor diagonal. This is analogous to the expressions in Eqs. (49) and (80). This state,  $\rho_{A,\text{out},1}$ , is effectively the “in” state for any subsequent collision between  $A$  and any other particle  $B_2$ :

$$\rho_{\text{in},2} = \rho_{A,\text{out},1} \otimes \rho_{B,\text{in},2} \quad (94)$$

Since we have just seen that  $\rho_{A,\text{out},1}$  is neither pure nor diagonal, the corresponding factorization into  $\rho_{R2} \times \rho_{C2}$  is impossible, and one has to resort to such procedures as used to derive Eqs. (80)–(85), or (87), and cross sections cannot be used to deduce the result.

To recover the standard kinetic theory one would be obliged to discard the off-diagonal elements of the matrix  $\rho_{A,\text{out}}$  after every collision, so that particle  $A$  appears to have been reprepared in a state appropriate for another good cross section encounter with the next target.

The situation here visualized is a particularly dramatic example of the “paradox” surrounding the once fashionable nonsense about the “collapse of the wave function.” When particle  $A$  has been scattered by  $B_1$  and then observed to collide with  $B_2$ , which presumably was prepared in a packet remote from the unscattered part of the  $A$  state after the first collision, it would seem convenient from the standpoint of ordinary scattering theory to obliterate this unscattered part of the  $A$  state and look at the second collision with a redesigned incident  $A$  packet. We might even imagine a Maxwell demon who could follow each molecule of a gas and reprepare

each pair after every collision, replacing its emerging state by  $\rho_A(t) \otimes \rho_B(t)$ , where

$$\rho_A(t) = \text{Tr}_B \rho_{AB}(t) \quad \text{and} \quad \rho_B(t) = \text{Tr}_A \rho_{AB}(t) \quad (95)$$

This would permit each particle to be ready for another routine collision. Every such reparation would destroy correlations and increase the entropy, and would in effect be the quantum mechanical analog of Boltzmann's old *Stosszahlansatz*, which postulated the reestablishment of randomness at each collision. These comments also recall the once popular assumption of random phases, which allowed one to ignore the off-diagonal elements of the density matrix in certain representations despite the fact that their actual values as determined by the exact quantum dynamical equations would generally be nonzero. In this way  $\rho_{AB}$  could be forced at all times to have the factored form  $\rho_A \otimes \rho_B$ . However, even though this procedure may be an acceptable approximation in cross-section calculations, it would clearly be an inappropriate subterfuge in the context of a fundamental theory concerning the long-term history of an assembly of interacting systems.

A rigorous quantum theory of the behavior of a gas of molecules will of course refuse to accept the services of any such demon. One might at most imagine some practically superhuman preparation at time zero in which there would be free particles in mutually dispersion-matched Gaussian wave packets headed for close interactions, so that every first pair collision would follow conventional scattering theory. Even with such elaborate preparation, however, subsequent states will no longer match, wave packets will become mixed, and it cannot take many sequential interactions before all the wave packets of all the particles will fill the entire enclosure surrounding the system in a bewildering pattern. Moreover, if we are to trust the general quantum mechanical theorem that every interaction is unitary, the global statistical operator is still a pure case with zero entropy. Only the intervention of the demon can alter that! We interpret these considerations as supportive of the conclusion that while ingenious applications of standard collision theory may seem to explain certain irreversible phenomena and to be compatible with the second law of thermodynamics, such theories are really in direct conflict with the basic postulates of quantum mechanics.

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