tion.

The following empirical relation was proposed by Toxen[4]:

$$-\left(\frac{dH_c}{dT}\right)_{T_c}\frac{T_c}{H_0}\bigg|_{\text{expt}}=\frac{\Delta(0)}{kT_c}\simeq\alpha. \qquad (3)$$

In Fig. 1, $\alpha^{-1}F(\alpha)$ is plotted as a function of α for the range of interest. Also plotted are the experimental points of $-(dH_c/dT)_{T_c}(T_c/H_0)[\Delta(0)/kT_c]^{-1}$ vs $\Delta(0)/kT_c$. The experimental data are those quoted by Toxen except for more recent data on lead[5] and niobium.[6] Toxen's relation is shown in the figure by a dashed line.

It can be seen that there is a reasonable agreement between the experimental points and our calculated curve, which is not surprising in view of the known[2] insensitivity of Lewis's method to the precise form of C_S chosen. From the figure we note that for α between 1.55 and 1.85, $F(\alpha)=\alpha\pm5\%$. This is the range within which most experimental values of α lie. It is our contention that this numerical property of $F(\alpha)$ accounts for the correctness of Toxen's relationship [Eq. (3)]. For $\alpha<1.55$ or $\alpha>1.85$ we expect that $(dH/dT)_{T_c}(T_c/H_0)[\Delta(0)/kT_c]^{-1}$ would follow our curve, and that they would depart from the dashed line describing Toxen's relation. The experimental points available do show this trend, indicating, we believe, that Toxen's relation is a numerical coincidence (though a strikingly good one).

We would like to thank Professor A. Ron and Mr. A. Lonke for helpful discussions.

[1]H. W. Lewis, Phys. Rev. 102, 1508 (1955).

[2]M. R. Schafroth in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 10.

[3]We remark that approximating $C_S(T)$ by a simple exponential is, crudely speaking, equivalent to considering the energy gap as independent of temperature (up to T_c). To obtain a better approximation for the experimental C_S we should write $\alpha=\langle\Delta(T)\rangle/kT_c$, where $\langle\Delta(T)\rangle$ is an "average" gap. One thus expects that $\alpha\simeq(1-\delta)\Delta(0)/kT_c$, where δ is some small positive number ($\delta\approx0.1$–0.2). This can be used to improve the agreement between our curve of Fig. 1 and the experimental points of $\Delta(0)/kT_c$.

[4]A. M. Toxen, Phys. Rev. Letters 15, 10, 462 (1965).

[5]J. D. Leslie and D. M. Ginsberg, Phys. Rev. 133, A362 (1964).

[6]E. R. Dobbs and J. M. Perz, in Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1963).

EXTENSIONS OF THE MOMENTUM-TRANSFER THEOREM*

E. Gerjuoy

University of Pittsburgh, Pittsburgh, Pennsylvania

(Received 22 November 1965)

Recently Lippmann,[1] in this Journal, has discussed the extension of the momentum-transfer theorem[2,3] to systems more complicated than the (elastic or inelastic) collisions of electrons with atomic hydrogen. Lippmann[1] also discussed extensions of the theorem to other observables, so as to derive, e.g., an energy-transfer theorem. In his discussion, Lippmann took exception to some remarks concerning the validity of the symbolic methods customarily employed in scattering theory. These remarks, from a preprint version of the paper which proved the momentum-transfer theorem for e-H collisions, were accurately quoted by Lippmann, but do not appear in the actually published paper,[3] because I already had decided the remarks were not wholly defensible.[4] Nevertheless there remain some differences between Lippmann's and my views of the status of the momentum-transfer theorem and its extensions. Making these differences explicit is the primary objective of this Letter.

In Lippmann's derivation of the momentum-transfer theorem, the starting point is

$$(\Psi^{(+)},\ [p_{1z}H-Hp_{1z}]\Psi^{(+)}), \qquad (1a)$$

the "expectation value" of the commutator between the Hamiltonian H and p_{1z}, the momentum operator (along its incident direction) of the incident particle. Lippmann relates (1a) to the momentum-transfer cross section via symbolic methods. My starting point has been much the same as Lippmann's, namely, the

identity

$$(\Psi^{(+)},\ p_{1z}H\Psi^{(+)})-(H\Psi^{(+)},\ p_{1z}\Psi^{(+)})=0. \qquad (1b)$$

On the other hand, I have chosen to evaluate the integrals on the left side of (1b) in a particular representation, the coordinate representation. In this representation, the terms in (1b) independent of the potential V are related, via Green's theorem, to a surface integral at infinity, which then can be evaluated from the known asymptotic behavior of $\Psi^{(+)}$ at large interparticle distances.

For the case of potential scattering, the aforementioned surface integral reduces immediately[2] to the physical momentum-transfer cross section, thus yielding the momentum-transfer cross-section theorem. The situation is less simple in e-H collisions, however, wherein $\Psi^{(+)}$ must be symmetric (singlet scattering) or antisymmetric (triplet scattering) under interchange of $\vec{r}_1$ and $\vec{r}_2$, the coordinates, respectively, of the indistinguishable "initially incident" and "initially bound" electrons. In this event, the surface integral (now over the five-dimensional boundary of the sphere at infinity in the six-dimensional space of $\vec{r}_1, \vec{r}_2$) reduces to the momentum-transfer cross section plus terms proportional to $\int d\vec{r}_1 \varphi_j^*(\vec{r}_1)p_{1z}\times\varphi_j(\vec{r}_1)$ integrated over all $\vec{r}_1$, where φ_j is the eigenfunction of atomic hydrogen in its jth bound state. Such terms, discussed in connection with Eqs. (G-42)-(G-44b), apparently are absent from[1] Eq. (L-6). But, because p_z has odd parity, these terms proportional to $(\varphi_j, p_z\varphi_j)$ vanish. At least superficially, therefore, Lippmann's version of the momentum-transfer theorem for e-H collisions agrees with mine.

Next, let p_1^2 replace p_{1z} in (1a) and (1b). Then proceeding from (1b) just as in Eqs. (G-36)-(G-49), one finds for singlet or triplet e-H collisions that the energy-transfer cross section σ_E is given by

$$\sigma_E=\frac{1}{2ik_0^3}\frac{2m}{\hbar^2}\int d\vec{r}\,\Psi^{(+)*}[\Psi^{(+)}\nabla_1^2V+2\nabla_1V\cdot\nabla_1\Psi^{(+)}]$$

$$-\frac{\sigma}{\hbar^2k_0^2}\int d\vec{r}_1\,\varphi_0^*(\vec{r}_1)p_1^2\varphi_0(\vec{r}_1)+\sum_j\frac{\sigma_j}{\hbar^2k_0^2}\int d\vec{r}_1\,\varphi_j^*(\vec{r}_1)p_1^2\varphi_j(\vec{r}_1), \qquad (2)$$

where the definition of σ_E is

$$\sigma_E=\frac{1}{k_0^2}\sum_j(k_0^2-k_j^2)\sigma_j+(k_0^2-k_1'^2-k_2'^2)\sigma_{\text{ion}}\,. \qquad (3)$$

In Eqs. (2) and (3), k_0 is the wave number of the incident electron; k_j is the wave number of the out-going electron after a collision leaving the atom in its jth bound state; $\vec{k}_1', \vec{k}_2'$ are the wave vectors of the out-going electrons when ionization occurs; σ is the total cross section, including ionization; σ_j is the cross section (including direct and exchange processes) for collisions producing out-going electrons with wave number k_j; σ_{ion} is the cross section for ionization, integrated over all allowed values of k_1', k_2'; and the sums over j include elastic scattering, $j=0$. Of course,

$$k_0^2-k_j^2=-\frac{2m}{\hbar^2}(\epsilon_0-\epsilon_j),\qquad k_0^2-k_1'^2-k_2'^2=-\frac{2m}{\hbar^2}\epsilon_0, \qquad (4)$$

where ϵ_j is the (negative) energy of the jth bound state.

Equation (L-7) apparently lacks the last two terms in Eq. (2) above. These terms, which correspond to the terms proportional to $(\varphi_j, p_z\varphi_j)$ in the momentum-transfer theorem, now do not vanish because p_1^2 has even parity. Thus, in the case of e-H collisions, Lippmann's result for the energy-transfer theorem disagrees (superficially, at least) with the result of a detailed calculation in the coordinate representation.

This apparent disagreement between Lippmann's and my version of the energy-transfer theorem persists even when the particles 1 and 2 are considered distinguishable, i.e., when $\Psi^{(+)}$ is not symmetrized. To be specific, in this situation

$$\sigma_E=\frac{1}{2ik_0^3}\frac{2m}{\hbar^2}\int d\vec{r}\,\Psi^{(+)*}[\Psi^{(+)}\nabla_1^2V+2\nabla_1V\cdot\nabla_1\Psi^{(+)}]-\frac{1}{\hbar^2k_0^2}\sum_j\sigma_j^{\text{exch}}\left[\hbar^2k_0^2-\int d\vec{r}_1\,\varphi_j^*(\vec{r}_1)p_1^2\varphi_j(\vec{r}_1)\right], \qquad (5)$$

where σ_j^{exch} is the exchange cross section for production of free particles 2, leaving the initially free incident particle 1 in the jth bound state. In Eq. (5), because the particles now are distinguishable, σ_E is defined not by Eq. (3) but rather by

$$\sigma_E = \frac{1}{k_0^2}\left[\sum_j (k_0^2 - k_j^2)(\sigma_j - \sigma_j^{\text{exch}}) + \int d\vec{k}_1' d\vec{k}_2' (k_0^2 - k_1'^2)\sigma_{\text{ion}}(\vec{k}_1', \vec{k}_2')\right], \quad (6)$$

where the total ionization cross section σ_{ion} satisfies

$$\sigma_{\text{ion}} = \int d\vec{k}_1' d\vec{k}_2' \sigma_{\text{ion}}(\vec{k}_1', \vec{k}_2').$$

Evidently Eq. (6) supposes that the kinetic energies of outgoing free particles 1 only—not of particles 2—will be measured and compared with the initially incident kinetic energy. Eq. (6) is not the only physically sensible possible definition of σ_E in (5), but no definition of σ_E will eliminate the expectation values $(\varphi_j, p^2\varphi_j)$ in the energy-transfer theorem unless such expectation values explicitly are incorporated into the definition of σ_E. For actual e-H collisions, involving indistinguishable particles, Eq. (3) provides the only physically sensible definition of σ_E.

The presence of the expectation values $(\varphi_j, p^2\varphi_j)$ in Eq. (5) is understandable. Whether or not the particles are indistinguishable, i.e., whether or not $\Psi^{(+)}$ is symmetrized, the surface integral arising from Eq. (1b) (with p_1^2 replacing p_{1z}) represents the net flux of probability current—weighted by p_1^2—across the sphere at infinity in $\vec{r}_1, \vec{r}_2$ space; the presence of forces, contained in the first term on the right side of (5) or (2), causes this net weighted flux to differ from zero. All collision processes, including those which convert 1 from a free to a bound particle, are included in the net probability current flux; but any physically sensible definition of σ_E, e.g., Eq. (6) or (3), corresponding to actually feasible measurements, should involve the kinetic energy fluxes of free (unbound) particles only. Consequently, only in the circumstances that particle 1 is always free, or that p_1^2 is expected to vanish whenever particle 1 is not free, does one expect σ_E of Eq. (6) to equal exactly the force terms involving V on the right side of (5). In fact, the extra terms in (5), proportional to σ_j^{exch}, have precisely the form one expects (in terms of the cross sections) for the rate at which the forces are causing a flow of p_1^2 from unbound to bound states of 1.

For actual e-H collisions, where the particles are indistinguishable, the precise form of the extra terms involving $(\varphi_j, p^2\varphi_j)$ is less readily interpreted physically, but it is clear that the genesis of these extra terms in (2) is essentially the same as in (5). The preceding paragraph also clarifies the fact that the vanishing expectation values $(\varphi_j, p_z\varphi_j)$ appear in the derivation of the momentum-transfer theorem, and suggests that extra terms involving the expectation values $(\varphi_j, A\varphi_j)$ will have to be included in the transfer theorem for any even-parity operator A, e.g., the angular-momentum transfer theorem, Eq. (L-8). However, I have not examined the angular-momentum transfer theorem, or the transfer theorem for any other even-parity operator A, in the detail that I have examined the energy-transfer theorem.

It is to be noted that the presence of extra terms involving $(\varphi_j, A\varphi_j)$ implies that the transfer theorem for A—unlike the momentum-transfer theorem—has little chance of being generally useful. For instance, granting exact knowledge of V, prediction of σ_E from (2) or (5) requires accurate knowledge of σ_j and the associated expectation values $(\varphi_j, p^2\varphi_j)$. Hence use of (2) or (5) to estimate σ_E generally will be no easier or more accurate than direct employment of the corresponding defining equations (3) or (6). For this reason the energy-transfer theorem and similar obvious extensions of the momentum transfer theorem were not included in my paper on e-H collisions.[3]

On the other hand, it is possible to eliminate the extra terms involving $(\varphi_j, A\varphi_j)$ in special cases. One important such case is the energy-transfer theorem for Coulomb interactions, i.e., just the case for which (2) was derived. In this case we know from the virial theorem that

$$\frac{1}{2m}\int d\vec{r}_1\, \varphi_j^*(\vec{r}_1) p_1^2 \varphi_j(\vec{r}_1) = -\epsilon_j. \quad (7)$$

Recalling Eqs. (3) and (4), using (7) converts Eq. (2) to

$$2\sigma_E = \frac{1}{2ik_0^3}\frac{2m}{\hbar^2}\int d\vec{r}\, \Psi^{(+)*}[\Psi^{(+)}\nabla_1^2 V + 2\nabla_1 V\cdot\nabla_1\Psi^{(+)}]. \quad (8)$$

Thus in the special case of e-H collisions there is a useful energy-transfer theorem, but (superficially at least) it differs by exactly a factor 2 from Lippmann's version. The result (8) suggests that the energy-transfer theorem remains useful—though differing by a numerical factor from Lippmann's version—in the collisions of many-particle systems interacting via Coulomb forces, e.g., in atom-atom collisions. The same comment should hold for any collisions wherein the virial theorem is applicable, e.g., to the collisions of many-particle systems interacting via homogeneous potentials of any degree n (if any case other than the Coulomb $n=-1$ actually exists).

Admittedly the coordinate representation proofs—of the momentum-transfer theorem published previously,[3] and of the energy-transfer theorem outlined here—become awkward and inelegant when extended to collisions more complicated than e-H. By finding the route to short elegant proofs for arbitrarily complicated colliding systems, Lippmann has made an important contribution therefore. This Letter has indicated, however, that the symbolic methods he employs must be made more precise before the extensions of the momentum-transfer theorem to arbitrarily complicated colliding systems, and to other observables, can be regarded as more than "plausible." In particular (concentrating now on the energy-transfer theorem), for many-particle systems including both distinguishable and indistinguishable particles, it is at least necessary to establish (a) the connection between the right-hand side of Eq. (L-7) and the physically sensible σ_E, and (b) the presence of the extra terms involving $(\varphi_j, p^2\varphi_j)$, which are not obviously explicitly manifested (though very likely contained) in Eqs. (L-7) and (L-9).

*Work supported by the Office of Naval Research.

[1]B. A. Lippmann, Phys. Rev. Letters 15, 11 (1965). Equation numbers referring to this paper are preceded by L.

[2]E. Gerjuoy, J. Math. Phys. 6, 993 (1965).

[3]E. Gerjuoy, J. Math. Phys. 6, 1396 (1965). Equation numbers referring to this paper are preceded by G.

[4]Regrettably, Lippmann did not check with me before publishing his Letter.

GENERALIZED EHRENFEST THEOREM*

B. A. Lippmann
Defense Research Corporation, Santa Barbara, California
(Received 17 December 1965)

In this note, we wish to show that the generalized Ehrenfest theorem[1] offers a new and useful approach to the theory of multichannel collisons. In particular, the theorem provides a natural connection between the mathematical and physical descriptions of the collision process, and it enables the resolution of the scattered amplitude in any channel to be effected quite readily.

We illustrate this by applying the theorem to a collision process involving N channels. The separation of the Hamiltonian in channel 1 and the basis vectors defined by this separation are

$$H=H_{0,1}+V,\quad H_{0,1}\Phi_{a,1}=E_a\Phi_{a,1}. \tag{1}$$

Other channels are denoted by replacing the subscript 1 by 2, 3, ..., N.

Assuming that channel 1 is the incident channel, the state vector is

$$\Psi_{a,1}^{(+)}=\Phi_{a,1}+\frac{1}{E_a+i\epsilon-H_{0,1}}V_1\Psi_{a,1}^{(+)}. \tag{2}$$

The first term on the right corresponds to the initial state; the scattered states are contained in the second term. Physically, this equation is interpreted as follows. It describes the scattering of a wave packet having an energy spread $\sim\epsilon$ around E_a. As the wave packet is made longer, it becomes more nearly monoenergetic ($\epsilon\to 0$).

The generalized Ehrenfest theorem examines the rate of change, induced by a collision process, in the expectation value, over a wave packet, of an observable A_c, defined in channel c. By relating the rate of change to a certain closed expression, the theorem in essence derives a sum rule for the process.

The expectation value of the rate of change