Lifetime Matrix in Collision Theory*

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(Received October 16, 1959)

The duration of a collision is usually a rather ill-defined concept, depending on a more or less arbitrary choice of a collision distance. If the *collision lifetime* is defined as the limit, as $R\to\infty$, of the difference between the time the particles spend within a distance R of each other and the time they would have spent there in the absence of the interaction, a well-defined quantity emerges which is finite as long as the interaction vanishes rapidly enough at large R.

In quantum mechanics, using steady-state wave functions, the average time of residence in a region is the integrated density divided by the total flux in (or out), and the lifetime is defined as the difference between these residence times with and without interaction. Transformation properties require construction of the *lifetime matrix*, **Q**. If the wave functions ψ_i are normalized to unit total flux in and out through a sphere at $R\to\infty$, the matrix elements are

$$Q_{ij}=\lim_{R\to\infty}\left[\int^{r<R}\psi_i\psi_j^*d\tau-R(v_i^{-1}\delta_{ij}+\Sigma_k S_{ik}v_k^{-1}S_{jk}^*)\right]_{\text{Av}},$$

where the average value is taken to eliminate oscillating terms at large R, S_{ik} is an element of the unitary scattering matrix, **S**, and v_i is the velocity in the ith channel. **Q** is Hermitian; a diagonal element Q_{ii} is the average lifetime of a collision beginning in the ith channel. As a function of the energy **Q** is related to **S**: $\mathbf{Q}=-i\hbar\mathbf{S}\,d\mathbf{S}^\dagger/dE$; **Q** and **S** contain the same information, from complementary points of view. When **Q** is diagonalized, its proper values, q_{ii}, are the lifetimes of metastable states if they are large compared to $\hbar/E$; for a sharp resonance, the measured lifetime is the average of $q_{ii}(E)$ over a distribution in energy. The corresponding eigenfunctions, Ψ_i, are the proper functions to describe these metastable states. The causality principle appears directly from an inequality involving the integral expression for Q_{ii} or q_{ii}, and it is shown how some of its consequences for inelastic collisions can be deduced.

INTRODUCTION

It is surprising that the current mathematical apparatus of quantum mechanics does not include a simple representation for so eminently observable a quantity as the lifetime of metastable entities. Unlike other dynamical observables. for which corresponding operators are available, the lifetime is usually computed by various indirect devices—among these are Gamow's complex energy eigenvalue, the combination of the Heisenberg relation with the width of an energy resonance, and special wave-packet representations. There seems to be a widespread misapprehension, which I hope in this note to allay, that it is impossible in principle to obtain a lifetime by a simple procedure from a steady-state solution of the time-independent Schrödinger equation for a single energy E. The lifetime matrix, **Q**, which can be derived in a simple way from steady-state wave functions, fills this theoretical lacuna, and illuminates a connection between lifetimes of metastable states and scattering theory.

For the analysis of collision events, a well-developed tool is available in the scattering matrix, **S**. However, when the scattering event is not simple, but involves a metastable intermediate with a lifetime longer than some simple collision time (defined, for instance, by $2a/v_0$, where a is some collision distance and v_0 the initial velocity), analysis in terms of the scattering matrix may become difficult in practice, though it remains unique in principle. Experimentally, it is possible to cover an entire gamut: from simple scattering collisions, through cases where the trajectory of a transistory intermediate can be deduced, to the situation where the lifetime of a slowly decaying product is the principal thing observed. There is a certain complementarity between observations of scattering at one end of this range and observations of lifetime at the other. It is gratifying to find this complementarity reproduced in a functional relationship between the matrices **S** and **Q** as functions of the energy E, which shows that they both contain the same essential information, though from very different points of view.

The point of view that will be taken in deriving the matrix **Q** is that a lifetime, or delay-time, can be associated with every collision. Classically, if the interaction between two particles is known and the initial conditions of the collision (including the energy E_1 and the angular momentum L_1 in the center-of-mass system) are specified, it is possible to compute the time $t(R;E_1,L_1,\cdots)$ that the particles spend within any distance R of each other. To get a well-defined lifetime independent of R, we may take the limit as $R\to\infty$ after subtracting the time $t_0(R;E_1,L_1,\cdots)$ that the particles would have spent within R in the absence of the interaction. If the collision is inelastic, the time t_0 is the sum of two parts corresponding to an incoming trajectory with velocity v_1 and angular momentum L_1, and an outgoing one with v_2, L_2, each of them terminating at its point of closest approach to the center of mass. The *collision lifetime* is then defined as

$$\begin{aligned}Q_{\text{cl}}(E_1,L_1,\cdots)&=\lim_{R\to\infty}[t(R;E_1,L_1,\cdots)\\&\qquad-\tfrac{1}{2}t_0(R;v_1,L_1)-\tfrac{1}{2}t_0(R;v_2,L_2)]\\&=\lim_{R\to\infty}[t(R;E_1,L_1,\cdots)-R(v_1^{-1}+v_2^{-1})].\quad(1)\end{aligned}$$

* Work supported by Stanford Research Institute through funds administered by the Divisional Research Committee of the Physical Sciences Division.

This expression converges in general for interactions of shorter range than the Coulomb one.

Quantally, if we use a steady-state wave function to describe the scattering, a lifetime might be related to the time spent, on the average, near a scattering center, as determined by dividing the number of particles in some central region by the rate at which they are flowing in or out. When the boundary of the scattering region is sharply delimited, this gives an unambiguous definition, and elementary cases have sometimes been analyzed in this way.[1] A much more satisfactory general procedure, however, is to consider only the *excess* number of particles near the center, after subtracting the number that would have been present in the absence of the interaction; this excess will remain finite even if the integration is taken to infinity, provided the interaction vanishes rapidly enough at large distances. This excess, divided by the total flux in (or out) through a closed surface at large distance from the center of interaction, gives the lifetime we desire. (It will be remarked that the definition of the lifetime in terms of the ratio of particles trapped to flux in or out is reminiscent of the definition of the Q of an oscillating system in electromagnetic theory. It is this analogy which motivates the symbolism chosen.)

When multiple solutions of the Schrödinger equation exist for a single energy E, transformation requirements lead to the matrix $\mathbf{Q}$, the diagonal elements, Q_{ii}, of which are the lifetimes associated with the particular solutions ψ_i defined by an incoming wave in the ith channel.

What is apparently a very different definition of a delay-time associated with a collision has been deduced by Bohm,[2] Eisenbud,[3] and Wigner[4] from a wave-packet analysis. In the case of elastic scattering, which can be described by a simple phase-shift, η, they show that a suitable definition of a delay-time involves the energy-derivative of the phase-shift,

$$\Delta t = \hbar d\eta/dE. \tag{2}$$

It is gratifying to be able to prove that the delay-time defined in this way and the lifetime Q_{ii} are in fact identical. This proof provides the clue to a general relationship between the scattering matrix $\mathbf{S}$ and the lifetime matrix $\mathbf{Q}$.

It should occasion no surprise that the collision lifetimes Q_{ii} as defined here may have negative values. These arise physically either from reflection of the incident particle before it penetrates into a central region, or from its acceleration and swift passage through a region of negative potential; in either case, the density of particles in the central region is lower than it would be without the interaction, and the collision is over sooner. If the interaction has a finite range, it is possible to establish a simple lower bound for Q_{ii}, leading to an elementary proof of a theorem, established in a different way by Wigner,[4] related to the principle of causality. When the Q_{ii}'s are positive and large with respect to $\hbar/E$, we have a criterion for the existence of metastable states; in this case, separate metastable states are best defined by diagonalizing the matrix $\mathbf{Q}$, and the eigenvalues q_{ii} are the lifetimes of the separate states.

[1] See, for instance, V. Rojansky, *Elementary Quantum Mechanics* (Prentice-Hall, New York, 1938), p. 125; or G. Gamow, Z. Physik **51**, 204 (1928).

[2] D. Bohm, *Quantum Theory* (Prentice-Hall, New York, 1951), pp. 257–261.

[3] L. Eisenbud, dissertation, Princeton, June, 1948 (unpublished).

[4] E. P. Wigner, Phys. Rev. **98**, 145 (1955).

LIFETIME FOR A ONE-DIMENSIONAL ELASTIC COLLISION

To make this definition precise, consider a one-dimensional problem in the region $0<x<\infty$, represented by a Schrödinger equation with a potential function that vanishes at large x and becomes infinite at $x=0$. The wave function satisfying the equation for a positive energy E is $\psi(x)$; at $x=0$, it must satisfy the condition $\psi(0)=0$. At large x, ψ may be written in the asymptotic form,

$$_\infty\psi(x) = A(e^{-ikx} - e^{i\eta}e^{ikx}), \tag{3}$$

where $k^2=(2m/\hbar^2)E$, and η is the phase shift, which vanishes when there is no interaction ($V=0$ for all $x>0$). The probability density is then $\rho(x)=\psi^*(x)\psi(x)$, while the average density in the absence of the potential is $\bar{\rho}(x)=\langle_\infty\psi^*{}_\infty\psi\rangle=\lim_{L\to\infty}(1/L)\int_0^L{}_\infty\psi^*{}_\infty\psi dx=2AA^*$. The integrated excess density in the central region is

$$I(R)=\int_0^R[\psi^*(x)\psi(x)-\bar{\rho}]dx. \tag{4}$$

If the potential vanishes rapidly enough at large x, this integral remains finite as $R\to\infty$, but it includes an oscillating term, $-AA^*k^{-1}\sin(2kR+\eta)$. The oscillation can be eliminated by taking the average value of $I(R)$ as R increases.

$$\langle I\rangle \equiv \lim_{R\to\infty}\frac{1}{R}\int_R^{2R} I(R')dR'. \tag{5}$$

$\langle I\rangle$ is the excess number of particles in the central region. Its absolute magnitude depends on the normalization of ψ, but so does the magnitude of the inward or outward flux with which we wish to compare it. The inward flow, in particles per second, across a boundary at large x, is found by applying the flux operation to the incoming part of ψ or $_\infty\psi$, $\Phi=Ae^{-kx}$, and

$$F_+=\frac{\hbar}{2mi}\left(\Phi^*\frac{d\Phi}{dx}-\Phi\frac{d\Phi^*}{dx}\right)=-A^*Av. \tag{6}$$

The outward flux F_- is similarly defined in terms of $\Phi^*e^{i\eta}=A^*e^{i(kx+\eta)}$. If we write

$$F=-F_+=F_-, \tag{7}$$

we can define the average delay-time as

$$Q = \langle I \rangle / F. \tag{8}$$

It is usually convenient to normalize the wave function to unit inward and outward flux. This can be done by replacing (3) by the form

$$_{\infty}\psi = v^{-\frac{1}{2}}[e^{-ikx} - e^{i\eta}e^{ikx}]. \tag{9}$$

Using Eq. (9), $\bar{\rho} = 2/v$, and the lifetime is expressed simply by

$$Q = \lim_{R\to\infty} \left[\int_0^R (\psi^*\psi - 2/v)dx \right]_{\mathrm{Av}}. \tag{10}$$

[A slightly different formulation for the collision lifetime that might be considered in place of Eq. (10) is

$$Q' = \int_0^\infty (\psi^*\psi - {}_{\infty}\psi^*{}_{\infty}\psi)dx. \tag{11}$$

Q' differs from Q by a term which is important at low energy,

$$Q' - Q = -\tfrac{1}{2}\hbar E^{-1} \sin\eta. \tag{12}$$

The identity between Q and the lifetime expressed by Eq. (2), which will be proven below, and convergence difficulties with Q' in higher angular momentum states, suggest a preference for Q rather than Q'.]

CONNECTION BETWEEN Q AND THE PHASE SHIFT

Eisenbud,[3] Bohm,[2] and Wigner[4] have pointed out that a simple wave-packet description of a collision implies a delay-time of the magnitude

$$\Delta t = \hbar (d\eta/dE). \tag{2}$$

It is worth while repeating the argument briefly in the form given by Wigner, before proving the identity between Δt and Q in the one-dimensional case.

To discuss the motion of a wave packet, a time-dependent wave function is needed, composed of a sum of terms behaving asymptotically as $_{\infty}\psi(x,t) = {}_{\infty}\psi(x)e^{-i\nu t}$. It suffices to take a packet composed of two such terms, with frequencies $\nu \pm \Delta\nu$, wave numbers $k \pm \Delta k$, and phase-shift $\eta \pm \Delta\eta$. The wave packet is then represented, in the asymptotic region of large x where $_{\infty}\psi(x)$ has the form (9), by

$$\begin{aligned} {}_{\infty}\psi_{\mathrm{w.p.}}(x,t) = 2v^{-\frac{1}{2}}[&e^{-i(kx+\nu t)} \cos(x\Delta k + t\Delta\nu) \\ &- e^{i(kx-\nu t+\eta)} \cos(x\Delta k - t\Delta\nu + \Delta\eta)]. \end{aligned} \tag{13}$$

The first term in the brackets has a maximum when $x_{\max} = -t(d\nu/dk) = -vt$, and represents a particle moving inward at times $t<0$; the second term represents the particle moving outward at a later time, with

$$x_{\max} = vt - d\eta/dk. \tag{14}$$

Since $\eta = 0$ and $d\eta/dk = 0$ when there is no interaction, Eq. (14) shows that the interaction has delayed the particle by a time

$$\Delta t = v^{-1} d\eta/dk = \hbar d\eta/dE. \tag{15}$$

This delay-time is identical with Q. From the Schrödinger equation,

$$(H-E)\psi = (T+V-E)\psi = 0, \tag{16}$$

and its first derivative with respect to E,

$$(H-E)(\partial\psi/\partial E) - \psi = 0, \tag{17}$$

we find

$$\begin{aligned} \psi^* T\frac{\partial\psi}{\partial E} - \frac{\partial\psi}{\partial E} T\psi^* \\ = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial^2\psi}{\partial x\partial E} - \frac{\partial\psi}{\partial E}\frac{\partial\psi^*}{\partial x}\right) = \psi^*\psi. \end{aligned} \tag{18}$$

Since ψ^* and $\partial\psi/\partial E$ vanish at $x=0$, integration from 0 to R gives

$$\int_0^R \psi^*\psi dx = -\frac{\hbar^2}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial x\partial E} - \frac{\partial\psi}{\partial E}\frac{\partial\psi^*}{\partial x}\right)_R. \tag{19}$$

The right-hand side is to be evaluated at large R, where $\psi = {}_{\infty}\psi$ can be represented by (9), so

$$\begin{aligned} \frac{\hbar^2}{2m}\left(\frac{\partial_{\infty}\psi}{\partial E}\frac{\partial_{\infty}\psi^*}{\partial x} - {}_{\infty}\psi^*\frac{\partial^2{}_{\infty}\psi}{\partial x\partial E}\right)_R \\ = \hbar\frac{\partial\eta}{\partial E} + \frac{2}{v}R - \frac{\hbar}{2E}\sin(2kR+\eta). \end{aligned} \tag{20}$$

Comparing with (10), and noting that $\frac{1}{2}\hbar E^{-1} \times \sin(2kR+\eta)$ is just the term eliminated by the averaging of Eq. (5), we find, finally,

$$\begin{aligned} \hbar d\eta/dE = \int_0^R (\psi^*\psi - 2/v)dx \\ + \tfrac{1}{2}\hbar E^{-1}\sin(2kR+\eta) = Q. \end{aligned} \tag{21}$$

Before proceeding, it is convenient here to point out a corollary that will be suggestive later. If we write $S = e^{i\eta}$, we obtain the identity

$$Q = \hbar d\eta/dE = -i\hbar S^* dS/dE. \tag{22}$$

This expression is the proper one for generalization when $\mathbf{S}$ is the scattering matrix for inelastic collisions and $\mathbf{Q}$ the lifetime matrix.

ELASTIC COLLISIONS IN SPACE

In three-dimensional space, it is convenient to treat collisions with a well-defined angular momentum. If there are no inelastic collisions, one then obtains a separate lifetime, Q_{ll}, associated with each value of the angular momentum quantum number, l. It will be shown subsequently how these can be combined to give the lifetime appropriate to some mixed quantum state which is not well-defined as to angular momentum.

In the usual way, the wave function is written in spherical coordinates about the center of mass of the colliding system, $\psi_l(r,\theta,\phi)$. At large r, where the scattering interaction vanishes, this can be written as

$$_\infty\psi_l(r,\theta,\phi)=r^{-1}{}_\infty\phi_l(r)g_l(\theta,\phi), \tag{23}$$

where the angular functions $g_l(\theta,\phi)$ are orthogonal and normalized to unity over a sphere. The functions $_\infty\phi_l(r)$ can be expressed in terms of complex radial eigenfunctions for the angular momentum quantum number l, (I_l is not the Bessel function!)

$$_\infty\phi_l(r)=v^{-\frac{1}{2}}[I_l(kr)-e^{i\eta_l}I_l^*(kr)], \tag{24}$$

where

$$I_l(kr)=(kr)^l\frac{d}{d(kr)}[(kr)^{-l}I_{l-1}(kr)], \tag{25}$$

and

$$I_0(kr)=e^{-ikr}.$$

These functions are normalized to unit inward and outward flux through the surface of a sphere at large r. For any l, at sufficiently large r the average density falls off as $(2/vr^2)$. The simplest expression for the lifetime integral, analogous to Eq. (10), is therefore

$$Q_{ll}=\lim_{R\to\infty}\left[\int^{|r|<R}(\psi_l^*\psi_l-2/vr^2)d\tau\right]_{\text{Av}}, \tag{26}$$

where $d\tau$ is a volume element.

The lifetime, Q_{ll}, as thus defined, is equal to $\hbar(d\eta_l/dE)$. From the Schrödinger equations for ψ^* and $\partial\psi/\partial E$,

$$\psi^*\psi=\frac{\hbar^2}{2m}\nabla\left(\frac{\partial\psi}{\partial E}\nabla\psi^*-\psi^*\nabla\frac{\partial\psi}{\partial E}\right), \tag{27}$$

so

$$\int^{|r|<R}\psi_l^*\psi_l d\tau\approx\frac{\hbar^2}{2m}\left(\frac{\partial_\infty\phi_l}{\partial E}\frac{\partial_\infty\phi_l^*}{\partial r}-{}_\infty\phi_l^*\frac{\partial^2{}_\infty\phi_l}{\partial r\partial E}\right)_{r=R}$$

$$=\hbar(d\eta_l/dE)+(2R/v)-(\hbar/2E)\times\sin(2kR+\eta_l+\tfrac{1}{2}l\pi)+G_l/R, \tag{28}$$

where G_l/R is a remainder that vanishes with R^{-1}. Thus,

$$Q_{ll}=\hbar(d\eta_l/dE)=-i\hbar S_l^*(dS_l/dE), \tag{29}$$

where

$$S_l=e^{i\eta_l}.$$

We are now in a position to extend the definition of the lifetime to a mixed state, Γ, which is not well-defined as to angular momentum. The wave function for this state, ψ_Γ, may be expanded in terms of the orthogonal functions ψ_l,

$$\psi_\Gamma=\sum_l a_{\Gamma l}\psi_l; \tag{30}$$

to preserve the normalization of ψ_Γ to unit flux, we must have

$$\sum_l a_{\Gamma l}a_{\Gamma l}^*=1. \tag{31}$$

If we now define the lifetime for the collision Γ by an equation like (26), and substitute the expansion (30), we find

$$Q_{\Gamma\Gamma}=\int_V(\psi_\Gamma^*\psi_\Gamma-2/vr^2)d\tau$$

$$=\sum_l a_{\Gamma l}a_{\Gamma l}^*Q_{ll}. \tag{32}$$

With inelastic collisions, where the wave functions may not be orthogonal, this kind of transformation will lead us to introduce off-diagonal elements of the form Q_{ij}.

LOWER BOUND FOR Q

Wigner has shown[4] how to establish a lower bound for the energy derivative of the phase shift. He gives a simple proof depending on a property of the derivative matrix, **R**. The integral expression used here for Q_{ll}, and its identity with $\hbar(d\eta_l/dE)$, lead to another, particularly simple, demonstration of this lower bound.[5] With Wigner, we suppose that the interaction has a finite radius, a. The wave function, ψ_l, will differ from $_\infty\psi_l$ only for $x\leqslant a$, so we can write Q_{ll} in the form

$$Q_{ll}=\int^{r<a}\psi_l^*\psi_l d\tau-\left(\frac{2a}{v}\right)+\lim_{R\to\infty}\left[\int_a^R({}_\infty\phi_l^*{}_\infty\phi_l-2/v)dr\right]_{\text{Av}}. \tag{33}$$

The first integral is positive definite, and the second can be expressed in terms of the function $I_l(kr)=I_l(\rho)$, so

$$\hbar\left(\frac{d\eta_l}{dE}\right)=Q_{ll}\geqslant-\left(\frac{2a}{v}\right)+\left(\frac{\hbar}{2E}\right)\times\int_{ka}^{\infty}\{2[I_l^*(\rho)I_l(\rho)-1]-[e^{-i\eta_l}I_l^2(\rho)+e^{i\eta_l}I_l^{*2}(\rho)]\}d\rho. \tag{34}$$

When this is evaluated, the result is identical with Wigner's; for $l=0$, for instance,

$$Q_{00}=\hbar(d\eta_0/dE)\geqslant-2av^{-1}+\tfrac{1}{2}\hbar E^{-1}\sin(2ka+\eta_0). \tag{35}$$

The integral expression for the lifetime, Q, is thus seen to be naturally adapted to expressing the causality principle in quantum mechanics. It will be shown subsequently how this principle can be applied to inelastic collisions.

[5] A related proof has been given by E. Corinaldesi and S. Zienau, Proc. Cambridge Phil. Soc. **52**, 599 (1956).

INELASTIC COLLISIONS

When we come to inelastic collisions, the analysis in terms of the phase shift must give way to the more general scattering matrix, **S**, which is unitary if ψ is normalized asymptotically to unit flux in and out. (Often, **S** is symmetric as well, but we shall not need to depend on this.) If we denote the product wave function involving the internal coordinates of the colliding partners in the jth state by $\omega_j(\mathbf{s})$ and their internal energy by E_j, we can describe the asymptotic behavior of the approach phase of a collision beginning in that state by

$$\Phi_j = r^{-1} v_j^{-\frac{1}{2}} I_j(k_j r) g_j(\theta,\phi)\omega_j(\mathbf{s}), \tag{36}$$

where $k_j^2 = 2m\hbar^{-2}(E-E_j)$, and the single label, j, represents a set of quantum numbers including the angular momentum of the collision. The complete wave function, ψ_j, includes outgoing portions in a number of states, described by Φ_k^*, with amplitudes and phases given by the matrix **S**:

$$_\infty\psi_j = \Phi_j - \sum_k S_{jk}\Phi_k^*. \tag{37}$$

The functions ψ_j are then normalized so that the total inward and outward flux through a spherical surface at large R is unity; they are also flux-orthogonal, in the sense that the cross-terms in the total inward or outward flux matrix vanish, so that flux-normalization is retained under a unitary transformation.

The lifetime matrix can now be defined by the $(n+3)$ dimensional volume integral,

$$Q_{ij} = \lim_{R\to\infty}\left[\int^{|r|<R}\int^{|s|<R} \psi_i\psi_j^* d\tau_s d\tau_r - R\sigma_{ij}\right]_{\mathrm{Av}}, \tag{38}$$

where $R\sigma_{ij}$ represents the average behavior of the integral at large R, beyond the range of interaction:

$$\sigma_{ij} = \lim_{R\to\infty} R^{-1}\int^{|r|}\int^{|s|<R} {}_\infty\psi_i^* {}_\infty\psi_j d\tau_{r,s}$$

$$= v_i^{-1}\delta_{ij} + \sum_k S_{ik} v_k^{-1} S_{jk}^*. \tag{39}$$

If the collision includes the possibility of a reaction with exchange of partners, $A+B\to C+D$, the same expression holds, but the integral in (38) includes portions in the channels corresponding to $A+B$, with coordinates $\mathbf{r}$ and $\mathbf{s}$, and portions in channels corresponding to $C+D$, with coordinates $\mathbf{r}'$ and $\mathbf{s}'$. These coordinates must then be normalized in such a way as to be connected by an orthogonal transformation.[6]

The integral formulation of Q_{ij} is not limited to any specific asymptotic form of the wave functions, and only slight modification is required if the normalization to unit flux is abandoned. In that case, the right-hand side of (38) must be multiplied by $(F_{ii}F_{jj})^{-\frac{1}{2}}$, where F_{ii} is the total flux of the incoming or outgoing part of ψ_i through an $(n-2)$-dimensional surface as $R\to\infty$, and the integral expression must be used for σ_{ij} in Eq. (39).

The relationship between **Q** and the scattering matrix, **S**, can now be established. It suffices to discuss a two-dimensional case, with $x\geqslant 0$ the collision coordinate and y the coordinate of internal motion; generalization to other cases is straightforward. The asymptotic form of the wave functions at large x is given by (37) with

$$\Phi_j = v_j^{-\frac{1}{2}} e^{-ik_j x}\omega_j(y). \tag{40}$$

where the ω_j's are orthogonal and normalized to unity. By an application of the earlier argument involving Green's theorem and the Schrödinger equations for ψ_i and $\partial\psi_j^*/\partial E$, it is easy to see that

$$\int_0^R\int_{-\infty}^{\infty}\psi_i\psi_j^* dydx$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left[\frac{\partial\psi_j^*}{\partial E}\frac{\partial\psi_i}{\partial x} - \psi_i\frac{\partial^2\psi_j^*}{\partial x\partial E}\right]_{x=R} dy. \tag{41}$$

The right-hand side of (41), evaluated at large R, becomes

$$R\sigma_{ij} + i\hbar\sum_k S_{ik}(dS_{jk}^*/dE) - (i\hbar/2m)[v_i^{-2}S_{ji}^* e^{-2ik_iR} - v_j^{-2}S_{ij}e^{2ik_jR}] + G_{ij}/R. \tag{42}$$

Averaging over the oscillating terms as $R\to\infty$, we find

$$Q_{ij} = i\hbar\sum_n S_{in}(dS_{jn}^*/dE). \tag{43}$$

Using matrix notation and the fact that **S** is unitary ($\mathbf{SS}^\dagger = \mathbf{1}$), we see that

$$\mathbf{Q} = i\hbar\mathbf{S}d\mathbf{S}^\dagger/dE = -i\hbar(d\mathbf{S}/dE)\mathbf{S}^\dagger = \mathbf{Q}^\dagger, \tag{44}$$

showing that **Q** is Hermitian. In view of the conjugate relation between time and energy, we can identify the time operator $\mathbf{t} = -i\hbar\partial/\partial E$, and write (44) in the illuminating form[7]

$$\mathbf{Q} = -\mathbf{S}\mathbf{t}\mathbf{S}^\dagger = (\mathbf{t}\mathbf{S})\mathbf{S}^\dagger. \tag{45}$$

Formally, it is possible to invert (44) and compute **S** from **Q** as a function of E; the boundary condition is obtained from the facts that $\mathbf{S}\to\mathbf{1}$ and $\mathbf{Q}\to\mathbf{0}$ as $E\to\infty$. **S** then satisfies the integral equation

$$\mathbf{S} = \mathbf{1} - \frac{i}{\hbar}\int_E^\infty \mathbf{Q}(E')\mathbf{S}(E')dE', \tag{46}$$

which leads to an iterative expression for **S** in terms of **Q**.

LIFETIME MATRIX AND THE DELAY TIME MATRIX

In his thesis,[3] Eisenbud extended the wave-packet analysis of collision delay-times to inelastic collisions,

[6] See, for instance, G. Breit, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 41, Part 1, p. 41.

[7] I am indebted to Dr. B. A. Lippmann for this observation.

defining what may be called the delay-time matrix $\mathbf{\Delta t}$. A typical element of it, Δt_{ij}, is the delay in the appearance of the peak outgoing signal in the jth channel, after the injection of a pulse in the ith. By a wave-packet analysis like that of Eq. (13), it can be shown that

$$\Delta t_{ij}=\mathrm{Re}\,[-i\hbar(S_{ij})^{-1}dS_{ij}/dE]. \qquad (47)$$

This involves the imaginary part of the logarithmic derivative of a single element of $\mathbf{S}$, whereas $\mathbf{Q}$, by Eq. (44), involves what is in a sense a logarithmic derivative of the matrix $\mathbf{S}$ as a whole (since $\mathbf{S}^\dagger=\mathbf{S}^{-1}$).

The *average* delay experienced by a particle injected in the ith channel is easily computed using the wave-packet model. Since the particle has a probability $|S_{ij}|^2$ of emerging in the jth channel, it is delayed on the average

$$\langle\Delta t_{i\cdot\cdot}\rangle_{\mathrm{Av}}=\sum_j S_{ij}^*S_{ij}\Delta t_{ij} =\mathrm{Re}\,[-i\hbar\sum_j S_{ij}^*dS_{ij}/dE]=Q_{ii}, \qquad (48)$$

where the last equality depends on (44) and the fact that Q_{ii} is real. The particle description by wave-packets thus leads to the same average delay as our previous steady-state model.

TRANSFORMATION PROPERTIES AND THE EIGENVALUES OF Q

$\mathbf{Q}$, like $\mathbf{S}$, contains nonzero elements only when the corresponding transition is permitted by the dynamical conservation laws. The conservation of total angular momentum, for instance, means that $\mathbf{Q}$ commutes with the matrix $\mathbf{L}^2$. Likewise, if the interaction is such as to conserve some symmetry of the system, the nonzero off-diagonal elements of $\mathbf{Q}$ connect only states with the same symmetry, and $\mathbf{Q}$ may be said to commute with the symmetry operator.

A diagonal element of $\mathbf{Q}$, say Q_{jj}, is to be interpreted as the average delay time in a collision described by the wave function ψ_j. The off-diagonal elements are required if a transformation is made from the functions ψ_i to another description, say,

$$\chi_j=\sum_k A_{jk}\psi_k. \qquad (49)$$

In that case, if $\mathbf{A}$ is a unitary matrix normalization is preserved, and $\mathbf{Q}$ transforms to

$$\mathbf{R}=\mathbf{AQA}^\dagger, \qquad (50)$$

and the diagonal elements of R are the collision-lifetimes of the χ_j.

In the transformation (49), the asymptotic form of the wave function χ_j becomes

$${}_\infty\chi_j=\Phi_j'-\sum_k T_{jk}\Phi_k'^*,$$

where

$$\Phi_j'=\sum_k A_{jk}\Phi_k, \qquad (51)$$

and

$$\mathbf{T}=\mathbf{ASA}^{\dagger *}.$$

Under such a transformation, the integral formulation for $\mathbf{Q}$, (38), is invariant, provided $\boldsymbol{\sigma}$ is replaced by $\boldsymbol{\sigma}'=\mathbf{A}\boldsymbol{\sigma}\mathbf{A}^\dagger$. On the other hand, the simple connection (44) between $\mathbf{Q}$ and $\mathbf{S}$ is lost if the transformation $\mathbf{A}$ is dependent on the energy. Instead, we get the equation

$$\mathbf{R}=i\hbar[\mathbf{T}(d\mathbf{T}^\dagger/dE)+\mathbf{TA}^*(d\mathbf{A}^{\dagger *}/dE)\mathbf{T}^\dagger -\mathbf{A}(d\mathbf{A}^\dagger/dE)]. \qquad (52)$$

A particularly important transformation is the one that diagonalizes $\mathbf{Q}$. To the eigenvalues of $\mathbf{Q}$, q_{ii}, correspond a set of eigenfunctions Ψ_i. It is an obvious step to identify the q_{ii}, when large, with the exponential decay times of long-lived metastable states, which are described by the wave functions Ψ_i. From this point of view, other methods of computing such lifetimes may be considered as ways of approximating the q_{ii}. This description is equally applicable to a case where q_{ii} has a sharp resonance as a function of energy, or to one where $q_{ii}(E)$ may be a slowly varying function.

The eigenfunctions, $\Psi_i(E)$, which diagonalize $\mathbf{Q}(E)$, may be used to construct wave packets to give a more detailed description of any collision or decay process. A general time-dependent wave function $\psi(r,t)$ can be written in the form

$$\psi(r,t)=\int_0^\infty \sum_j a_j(E)\Psi_j(E,r)e^{-iEt/\hbar}dE. \qquad (53)$$

If this represents a decaying system, in general the states Ψ_j with short lifetimes q_{jj} will decay rapidly, and ultimately the wave function near the center of observation will be composed predominantly of the longest-lived term Ψ_0, which will thereafter decay with its proper lifetime q_{00}.

The transformation $\mathbf{B}$ that diagonalizes $\mathbf{Q}$ is itself a function of the energy, and $\mathbf{q}$ is related to the transform of $\mathbf{S}$ by an equation like (52). But if the Hamiltonian is real (neglecting spins and magnetic fields), the wave functions Ψ_i that diagonalize $\mathbf{Q}$ can be taken as real, and they are symmetric in their incoming and outgoing parts:

$${}_\infty\Psi_i=\sum_k (B_{ik}\Phi_k+B_{ik}^*\Phi_k^*). \qquad (54)$$

If $\mathbf{B}$ is known, $\mathbf{S}$ is fixed by

$$\mathbf{S}=-\mathbf{B}^\dagger\mathbf{B}^*, \qquad (55)$$

and the transform of $\boldsymbol{\sigma}$ is the real matrix $\boldsymbol{\rho}=\mathbf{B}\boldsymbol{\sigma}\mathbf{B}^\dagger$ with elements

$$\rho_{ij}=\mathrm{Re}\,[\sum_m B_{im}v_m^{-1}B_{mj}]. \qquad (56)$$

In this case, $\mathbf{T}=-\mathbf{1}$ simply, and Eq. (52) reduces to

$$\mathbf{q}=\mathrm{Re}\,(\mathbf{B}\mathbf{t}\mathbf{B}^\dagger). \qquad (57)$$

CAUSALITY RELATIONS FOR INELASTIC COLLISIONS

The causality relation (34) can be generalized to inelastic collisions by using the eigenfunctions Ψ_i and the diagonalizing transformation **B**. Again, it will be assumed that the interaction vanishes outside the distance a. With the definitions

$$M_{jk}=\int^{|r|<a}\int^{|s|<\infty}\Psi_j\Psi_k{}^*d\tau_s d\tau_r, \qquad (59)$$

and

$$N_{jk}=\delta_{jk}(\hbar/mv_j^2)\int_{k_ja}^{\infty}[I_j{}^*(\rho)I_j(\rho)-1]d\rho$$
$$+\sum_n S_{jn}S_{kn}{}^*(\hbar/mv_n^2)\int_{k_na}^{\infty}[I_n{}^*(\rho)I_n(\rho)-1]d\rho$$
$$-\lim_{R\to\infty}\left[S_{jk}(\hbar/mv_k^2)\int_{k_ka}^{k_kR}I_k{}^{*2}(\rho)d\rho\right.$$
$$\left.+S_{kj}{}^*(\hbar/mv_j^2)\int_{k_ja}^{k_jR}I_j^2(\rho)d\rho\right]_{\text{Av}}, \qquad (60)$$

the proper lifetimes q_{ii} become

$$q_{ii}=M_{ii}-a\rho_{ii}+(\mathbf{BNB}^\dagger)_{ii}, \qquad (61)$$

and when $i\neq j$,

$$M_{ij}=a(\mathbf{B}\sigma\mathbf{B}^\dagger)_{ij}-(\mathbf{BNB}^\dagger)_{ij}. \qquad (62)$$

A lower bound for each q_{ii} follows from the fact that M_{ii} is positive definite. Similar inequalities applying to the diagonal elements of **Q** can be obtained from the integral (38), and others result from (61) and (62). As a result, a set of inequalities involving the elements of **S** and $d\mathbf{S}/dE$ can be established.

PROPER LIFETIME AND OBSERVABLE DECAY LIFETIME

Up to now I have asserted that the proper lifetimes obtained by diagonalizing the matrix **Q** are to be identified with the exponential decay half-lives of metastable systems. This can be tested by a comparison with the well established formulas for a single sharp long-lived resonance in a simple quantum mechanical system.

If the resonance is centered at E_0 and the half-width of the level is Γ, the phase shift is given by

$$\eta=2\delta=2\delta^0+2\tan^{-1}[\Gamma/(E_0-E)], \qquad (63)$$

so

$$Q(E)=\hbar d\eta/dE=\hbar\Gamma[(E_0-E)^2+\Gamma^2]^{-1}. \qquad (64)$$

The half-life for decay is known to be

$$\tau=\hbar/2\Gamma, \qquad (65)$$

and it is seen that the value of Q at the resonance is twice this,

$$Q(E_0)=\hbar/\Gamma=2\tau. \qquad (66)$$

However, the lifetime that is observed in a decaying system cannot be characterized by the exact energy E_0, because the decaying state itself is not so well defined. The line shape formula gives the probability of finding the state with any given energy E near E_0; it is

$$P(E)=\Gamma/\pi[(E_0-E)^2+\Gamma^2]. \qquad (67)$$

Clearly, we may expect observation of the decay to give an average value of the lifetime,

$$\bar{Q}=\int_0^\infty P(E)Q(E)dE. \qquad (68)$$

When this is evaluated, our expectation is confirmed:

$$\bar{Q}=\hbar/2\Gamma=\tau. \qquad (69)$$

Equation (68) can be taken as a general expression for the expectation value of Q in a measurement of the decay lifetime. It applies not only to a sharply defined resonant state, but also to regions where the spectrum $Q(E)$ may be fairly smooth, and $P(E)$ may be determined by the conditions under which the metastable particles were formed.

It must not be thought that $Q(E)$ is experimentally meaningless for energies more sharply defined than $\Delta E=2\Gamma$. Finer detail can be measured experimentally by a steady scattering experiment lasting much longer than τ. The decay experiment is only one way of measuring the collision lifetime.

DISCUSSION

The lifetime matrix whose properties have just been deduced provides the possibility of classifying collisions in terms of the ratio of their lifetimes, Q_{ii}, to the quantity ($\hbar/2E$) which represents a specifically quantum resonance effect [see, for instance, Eqs. (34) and (35)]. Rapid collisions, with $2EQ_{ii}/\hbar\ll-1$, correspond to simple repulsion or to swift passage across a potential well; when the interaction has a finite range, an inequality like (34) sets a natural lower bound for this quantity. When $|2EQ_{ii}/\hbar|<1$, we are in the domain of quantal resonance effects. (Of course, there are often additional quantum effects in the central region of strong interaction.) When $2EQ_{ii}/\hbar\gg1$, it becomes meaningful to discuss the event in terms of metastable states of the compound particle, and it will often be convenient to classify these states in terms of the eigenfunctions Ψ_i which diagonalize **Q**, with the corresponding proper lifetimes, q_{ii}.

Outside the domain of peculiarly quantal effects, the lifetime Q_{ii} will be expected to approach a classical limit as E becomes large. This limit will be just the classical collision lifetime defined by Eq. (1).

In defining **Q**, we have thus far confined ourselves to short-range interactions. The Coulomb interaction, particularly, demands separate treatment. In this case, the classical lifetime, Q_{cl}, has a logarithmic divergence as $R\to\infty$, and this will be expected to persist in the quantum-mechanical treatment. Nevertheless, it is possible to define a meaningful relative lifetime in the case of a Coulomb collision distorted by an additional short-range interaction, by comparing the distorted collision with a pure Coulomb collision.

In both nuclear theory and chemical kinetics, the concept of a metastable compound particle as an intermediate in collision processes has been very fruitful. The lifetime matrix is particularly adapted to the discussion of such states. In nuclear reactions, it is well-known that the compound states exhibit sharp resonances at low energies, described by Bohr's compound nucleus theory, whereas at higher energies the cross sections vary more smoothly with energy. It is usual to describe this in terms of the overlapping of many neighboring broad resonances, but it is also permissible to describe this region in terms of one or more of the metastable states described by the wave functions Ψ_i that diagonalize the lifetime matrix. These functions, and their associated lifetimes q_{ii}, are naturally smooth functions of the energy, and may provide a useful alternative to the description in terms of overlapping resonances. Since they are exact solutions of the time-independent Schrödinger equation, they are well-defined at each energy E.

In terms of the wave functions Ψ_i, a typical collision can be described as follows: If the initial kinetic energy and angular momentum of the collision as well as the internal states of the colliding particles are well-defined, the collision is described by a wave function ψ_λ with an asymptotic form like Eq. (37). This wave function can also be analyzed in terms of the Ψ_i:

$$\psi_\lambda = \sum_i a_{\lambda i} \Psi_i. \tag{70}$$

If all the Ψ_i except one, say Ψ_k, have very short proper lifetimes, q_{ii} and q_{kk}, the collision will be observed to have a probability $P_\lambda' = \sum_{i \neq k} a_{\lambda i} a_{\lambda i}^*$ of leading to a simple scattering event, and a probability $P_{\lambda k} = a_{\lambda k} a_{\lambda k}^*$ of yielding a metastable compound particle with a lifetime q_{kk} and a mode of decay described by the outgoing asymptotic form of Ψ_k. If a metastable compound in the same state is formed by a different collision ψ_μ, the probability of formation $P_{\mu k} = a_{\mu k} a_{\mu k}^*$ will be different, but the lifetime and mode of decay will be the same. If, however, there exist two or more metastable states, Ψ_k and Ψ_m, with long lifetimes, different modes of collision will in general form them in different proportions, and the average lifetime and mode of decay will be observed to depend on the mode of formation of the compound state. Since the q_{ii}'s can be identified with exponential half-lives, a careful analysis of the decay curves in such a situation should show them to be composed of a superposition of two pure exponential decays in each case, with lifetimes q_{kk} and q_{mm}.

The collision lifetime, as defined in this note, is a characteristic property of any collision. For long-lived collisions, the lifetime becomes more accessible to measurement than other scattering properties; the lifetime matrix and its associated eigenfunctions become a suitable theoretical framework for discussing metastable states. As well as shedding light on some aspects of nuclear reactions, this description is immediately applicable to atomic and molecular collisions. Unimolecular chemical reactions, dissociation and ionization of long-lived excited states produced by electron or photon impact, and other molecular processes, can be described in the language of the lifetime matrix. In a relativistic formulation, the lifetime matrix should be equally useful for the description of higher energy events.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating conversations with Professor E. P. Wigner and Professor F. E. Low, who raised pertinent questions on aspects of this work.