can then be summed up in this way. The Hamiltonian matrix was effectively reduced to the form Eq. (D3). The first submatrix, $H^{(1)}-E$ corresponds to a simple operator, and represents a problem which can be solved exactly. The second submatrix, $H^{(2)}-E$ $(\mathfrak{K}-EQ)$, though more complicated, has the property that its spectrum is discrete below the inelastic threshold, and so it can readily be bounded. Consequently, in terms of an exact solution of $H^{(1)}$ and a bound on $H^{(2)}$ a bound is found on $k\cot(\eta-\theta)$.

PHYSICAL REVIEW VOLUME 130, NUMBER 1 1 APRIL 1963

Collision Lifetimes in Many-Body Processes*

FELIX T. SMITH
Stanford Research Institute, Menlo Park, California
(Received 26 November 1962)

Collision lifetimes and the lifetime matrix are expressly formulated so as to include three-body and many-body collision and breakup processes. The many-body states are expressed in the generalized angular momentum representation, in which the principal radial coordinate is proportional to the square root of the trace of the inertia tensor for the N-body configuration. The physical significance of the (energy-dependent) three-body collision lifetime $Q^{(3)}(E)$ is clarified by considering the special case where the three-body breakup occurs by way of a metastable two-body intermediate. If the metastable occurs with an internal energy E_m and a decay time τ_m, and the process creating it has a collision lifetime $Q^{(2)}(E-E_m)$, the connection with $Q^{(3)}$ is: $Q^{(3)}(E)=Q^{(2)}(E-E_m)+\tau_m E_m/E$. This result holds both classically and quantally.

A. INTRODUCTION

THE breakup of an unstable particle into three or more fragments is an important process in many areas of physics and chemistry: high-energy particles, compound nuclei, and highly excited molecules provide a variety of examples. The inverse process of three-body collision can also be important in chemical reactions and in the nuclear reactions of stellar interiors. The lifetime of the unstable particle or collision complex is one of its principal characteristics. It is the purpose of this note to examine some general features of such lifetimes when three-body processes are present.

For a two-body collision in the simplest case (elastic scattering, classical nonrelativistic mechanics, forces of range shorter than Coulomb), the collision lifetime is conveniently defined as the limit, as $R\to\infty$, of the difference between the time the particles spend within a distance R of each other in the actual collision and the time they would have spent there in a hypothetical trajectory without any interaction[1,2]:

$$Q_{\rm cl}=\lim_{R\to\infty}[t(R)-t_0(R)]. \quad (1)$$

This definition can be readily translated to quantum mechanics, and leads to the result that the collision lifetime is proportional to the energy derivative of the phase shift, and thus also to the statistical density of available states; for isolated resonances and slowly decaying states, there is a simple relation between the collision lifetime, the width of the resonance, and the characteristic decay time of the state.[3] The definition is also easily extended to inelastic collisions—in the quantal case there results the lifetime matrix $\mathbf{Q}$ related to the energy derivative of the scattering matrix $\mathbf{S}$.[1] Classically, the lifetime for an inelastic collision is defined by subtracting from the actual collision duration that of a hypothetical trajectory with two portions, the asymptotic incoming and outgoing paths extended as straight lines to their respective points of closest approach.

The development of a new description for three-body and many-body collisions[4] was initially motivated by a desire to include these processes in the formulation of the lifetime matrix. This note will carry out that program explicitly.

In treating three-body and $(N+1)$-body events, it is most helpful to use a center-of-mass coordinate system normalized so that all internal coordinates involve a common reduced mass $\mu^{(3)}$ or $\mu^{(N+1)}$ such that

$$\mu_{(3)}{}^2=\prod_{i=1}{}^3 m_i/\sum_{i=1}{}^3 m_i,$$
$$\mu_{(N+1)}{}^N=\prod_{i=1}{}^{N+1} m_i/\sum_{i=1}{}^{N+1} m_i. \quad (2)$$

The internal coordinates characterize a space of $3N$

* This work was supported principally by the National Science Foundation and in part by the National Aeronautics and Space Administration.

[1] F. T. Smith, Phys. Rev. **118**, 349 (1960), referred to below as "LM"; also **119**, 2098(E) (1960). See also A. Krzywicki and J. Szymanski, Progr. Theoret. Phys. (Kyoto) **23**, 376 (1960).

[2] Such a definition is implicit in L. Eisenbud, dissertation, Princeton, June, 1948 (unpublished) and E. P. Wigner, Phys. Rev. **98**, 145 (1955).

[3] T. Ohmura has pointed out an error of a factor of 2 in LM. The decay time τ_m is $\frac{1}{2}$ the average value $\bar{Q}$ near the resonance and $\frac{1}{4}$ the value $Q_{\max}$ at the resonance; physically this is reasonable since the average collision lifetime $\bar{Q}$ involves two passages through a barrier, while the decay time τ_m involves only one. [See also the Appendix in F. T. Smith, J. Chem. Phys. **36**, 248 (1962).]

[4] F. T. Smith, Phys. Rev. **120**, 1058 (1960), referred to below as "GAM"; See also L. M. Delves, Nucl. Phys. **9**, 391 (1958–1959).

dimensions in which there is a natural radial coordinate ρ_N (whose origin occurs where all interparticle distances are zero). Among other identities, ρ_N is given a simple physical significance by the fact that its square is proportional to the trace of the inertia tensor for the configuration of the N particles,

$$\mathrm{Tr}\mathbf{I}=I_t=\sum_{k=1}^{3}I_{kk}=2\mu_{(N+1)}\rho_N^2. \tag{3}$$

ρ_N is entirely analogous to the interparticle distance r for two particles, and can be called the interparticle (generalized) distance for $N+1$ particles. As the particles move ρ_N changes, and if they move without interaction their path traces a straight line in the $(3N)$-dimensional space. On this straight line is a point where ρ_N has a minimum value, say B_N; B_N is the generalized impact parameter for this trajectory.

Using these concepts, the classical collision lifetime can be readily defined for an event involving three or more particles. Consider, for example, a collision with two incoming and three outgoing particles, say $AB+C\rightarrow A+B+C$. The trajectory can be followed from an initial point where the distance from C to the center of mass of AB is R_1 to a final point where the three-body distance $\rho_2=R_2$; from the time $t(R_1,R_2)$ for this passage we subtract the time $\frac{1}{2}t_0(R_1)$ required to follow the asymptotic initial trajectory from R_1 to its extrapolated point of closest approach and the time $\frac{1}{2}t_0(R_2)$ to follow the asymptotic final trajectory out from its closest point to R_2. The lifetime is, then, the limit,

$$Q=\lim_{R_1,R_2\rightarrow\infty}\{t(R_1,R_2)-\tfrac{1}{2}t_0(R_1)-\tfrac{1}{2}t_0(R_2)\}. \tag{4}$$

Formally this is identical with the expression for two-body inelastic collisions, but it involves generalized distances instead of ordinary ones where three separate particles are involved.

In quantum mechanics, similarly, the expressions originally derived for two-body inelastic collision apply virtually unchanged to three-body events provided only that some of the definitions are appropriately generalized. The development will be carried out in some detail in a later section, since the detailed forms of the expressions will be useful.

It is often possible to avoid dealing directly with a three-body event if it can be broken down into a sequence of two-body events. For example, a collision complex (ABC) may break up first into C plus a metastable pair $(BC)_m$, with the metastable breaking up later after its characteristic decay time, τ_m. If τ_m is long enough, we can unambiguously separate these two events and determine the two-body lifetime $Q^{(2)}$ for the first stage process $AB+C\rightarrow A+(BC)_m$. Alternatively we can look at the three-body lifetime $Q^{(3)}$ for the over-all process, $AB+C\rightarrow A+B+C$. Since both of these descriptions are compatible and apply to the same total process, there is a relation between them which relates $Q^{(3)}$ to $Q^{(2)}$ and τ_m. This relation is helpful in providing additional physical understanding of $Q^{(3)}$. It will be derived in the next section, which is devoted to the argument in classical mechanics. Following that, the quantal translation of the same relation will be justified, and its extension to more complicated cases indicated. I, then, give the formal changes in LM necessitated by the introduction of many-body reactions, and show that the general theorems remain valid with little or no change.

B. CLASSICAL MECHANICS

1. General Formulation

It is convenient to describe both the two-body and the three-body states of the system (ABC) in terms of the normalized center-of-mass coordinates of GAM. These coordinates are such that the kinetic energy involves the unique reduced mass $\mu_{(3)}$ of Eq. (2): to accomplish this we represent the vector AB, for examply, by $\mathbf{r}_{AB}=(\xi_4',\xi_5',\xi_6')$ whose magnitude is not the simple distance d_{AB} between A and B, but the normalized distance

$$r_{AB}=|\mathbf{r}_{AB}|=\left(\frac{\mu_{AB}}{\mu_{(3)}}\right)^{1/2}d_{AB}=\left[\frac{m_Am_B}{\mu_{(3)}(m_A+m_B)}\right]^{1/2}d_{AB}; \tag{5}$$

similarly, the vector from C to the center of mass of AB is represented by $\mathbf{r}_C=(\xi_1',\xi_2',\xi_3')$, where r_C is related to the distance d_C from C to the AB center of mass by

$$r_C=\left(\frac{\mu_C}{\mu_{(3)}}\right)^{1/2}d_C=\left[\frac{m_C(m_A+m_B)}{\mu_{(3)}(m_A+m_B+m_C)}\right]^{1/2}d_C. \tag{6}$$

In the same way we can define $\mathbf{r}_{BC}=(\xi_4,\xi_5,\xi_6)$ and $\mathbf{r}_A=(\xi_1,\xi_2,\xi_3)$, and we find that the three-body distance $\rho=\rho_2$ defined by Eq. (3) is related to them by:

$$\rho^2=\rho_2^2=r_{AB}^2+r_C^2=r_{BC}^2+r_A^2. \tag{7}$$

The associated velocities must be normalized in the same way: For example,

$$\begin{aligned} v_A&=(\dot\xi_1^2+\dot\xi_2^2+\dot\xi_3^2)^{1/2},\\ v_{BC}&=(\dot\xi_4^2+\dot\xi_5^2+\dot\xi_6^2)^{1/2}, \end{aligned} \tag{8}$$

and

$$V=(v_A^2+v_{BC}^2)^{1/2}=(v_{AB}^2+v_C^2)^{1/2}=[2T/\mu_{(3)}]^{1/2}. \tag{9}$$

Using these coordinates and velocities, we can replace Eq. (4) by an expression involving the duration $t(R)$ of the trajectory inside the hypersphere $\rho\leq R$, and the hypothetical durations inside R of the initial and final trajectories, $t_i(R)$ and $t_f(R)$:

$$Q=\lim_{R\rightarrow\infty}\{t(R)-\tfrac{1}{2}t_i(R)-\tfrac{1}{2}t_f(R)\}. \tag{10}$$

If we are looking at the process $AB+C\rightarrow A+B+C$ the time $\frac{1}{2}t_i(R)$ is determined by the initial velocity v_{Ci} and impact parameter B_{Ci} associated with the motion of the

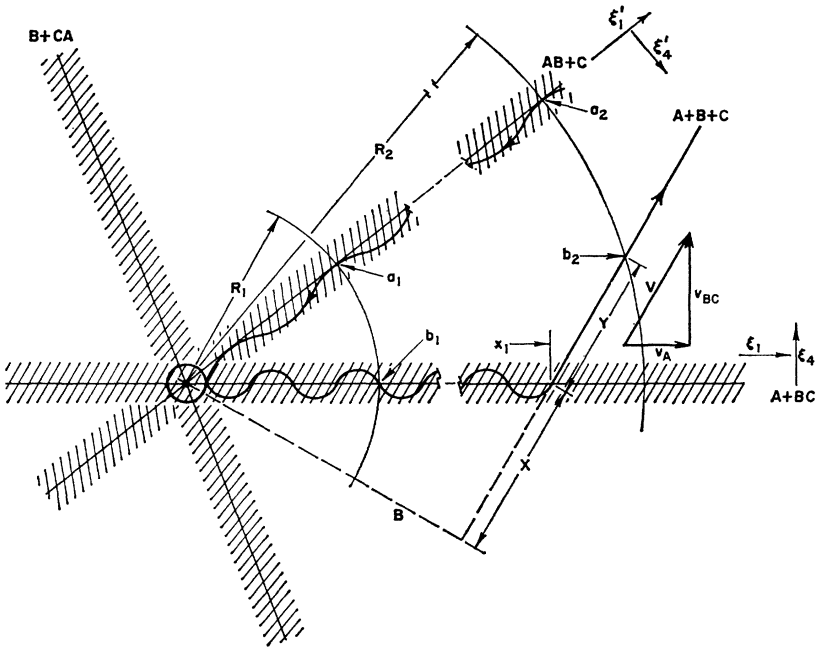

FIG. 1. A trajectory for the process $AB+C \rightarrow (ABC) \rightarrow A+(BC)_m \rightarrow A+B+C$.

vector $\mathbf{r}_C$,

$$\tfrac{1}{2}t_i(R)=v_{Ci}^{-1}(R^2-B_{Ci}^2)^{1/2} = (R/v_{Ci})-(B_{Ci}^2/2Rv_{Ci})+\cdots. \quad (11)$$

On the other hand, the final trajectory involves the velocity V_f and generalized impact parameter $B_{2,f}$ in the space of the six-dimensional vector ϱ, so that

$$\tfrac{1}{2}t_f(R)=v_f^{-1}(R^2-B_{2,f})^{1/2}=(R/V_f)-(B_{2,f}^2/2RV_f). \quad (12)$$

In the limit the higher terms in the expansion can be ignored, and Eq. (10) becomes

$$Q=\lim_{R\rightarrow\infty}\{t(R)-R(v_{Ci}^{-1}+V_f^{-1})\}, \quad (13)$$

in entire analogy to Eq. (1) of LM.

2. Participation of Intermediate Binaries

There are many cases where three-body collisions or breakup appear to occur through an intermediate stage consisting of one free particle and a metastable pair. In other cases, a purely three-body event occurs, and no two-body intermediate can be detected. The distinction between these two types of three-body collision was discussed in GAM. The one involving a binary intermediate is particularly instructive in connection with three-body lifetimes, since it can be looked at either as an over-all three-body process with a three-body lifetime, or as a sequence of two-body events with well-defined two-body lifetimes. The connection between these two points of view will be examined here.

Consider the process

$$AB+C \rightarrow (ABC) \rightarrow A+(BC)_m \rightarrow A+B+C. \quad (14)$$

A characteristic trajectory for such a process is plotted in the plane (ξ_1,ξ_4) in Fig. 1; the figure is constructed in the manner described in GAM. The full three-body lifetime $Q^{(3)}$ is obtained classically if you apply Eq. (10) using a large enough value of R, say R_2 in Fig. 1. If v_A is the normalized relative velocity of A and $(BC)_m$, and τ_m is the decay lifetime of $(BC)_m$, this requires

$$R_2 \gg x_1 = v_A\tau_m. \quad (15)$$

On the other hand, the process will fall into the distinct portions represented in Eq. (14) provided $x_1 \gg d$, where d is the characteristic range of the three-body interaction region. In that event, the initial portion of the process, leading to the metastable, is characterized by the two-body collision lifetime of the passage through complex (ABC), $Q^{(2)}$. This can often be defined quite well by an expression like Eq. (10) without strictly letting $R \rightarrow \infty$, but using instead a sufficiently large value, say R_1 in Fig. 1, such that

$$x_1 \gg R_1 \gg d. \quad (16)$$

The metastable $(BC)_m$ is characterized not only by its own lifetime τ_m, but also by its energy E_m which is released when it breaks up. In Fig. 1, we can assume that all this energy appears as the velocity v_{BC}:

$$2E_m/\mu = v_{BC}^2. \quad (17)$$

The total energy of the final products $A+B+C$ is

$$E=\tfrac{1}{2}\mu V^2=\tfrac{1}{2}\mu(v_A^2+v_{BC}^2). \quad (18)$$

It is convenient to consider the lifetimes as functions of the kinetic energy of the final rather than the initial state, so that $Q^{(2)}$ depends on $(E-E_m)$.

We can now apply Eq. (10) to find $Q^{(3)}(E)$ in terms of $Q^{(2)}(E-E_m)$ and τ_m. If all the interaction distances are small compared to R_1 and R_2, we have

$$Q^{(2)}(E-E_m)=t(a_1,b_1)-R_1(v_{Ci}^{-1}+v_A^{-1}), \quad (19)$$

where v_{Ci} is the normalized relative initial velocity of $AB+C$. On the other hand,

$$Q^{(3)}(E)=t(a_2,b_2)-t_0(a_2,b_2), \quad (20)$$

where

$$t(a_2,b_2)=t(a_1,b_1)+(1/v_{Ci})(R_2-R_1)+(1/v_A)(x_1-R_1)+Y/V, \quad (21)$$

and

$$t_0(a_2,b_2)=R_2/v_{Ci}+(1/V)(X+Y). \quad (22)$$

Substituting, and using

$$x_1=v_A\tau_m$$

and

$$X=x_1v_A/V=v_A^2\tau_m/V, \quad (23)$$

we find the final result

$$Q^{(3)}(E)=Q^{(2)}(E-E_m)+\tau_mE_m/E. \quad (24)$$

The derivation of Eq. (24) has been carried through with the aid of a diagram suited to illustrating classical trajectories for the collinear motion of the particles. It is easy to see that no changes of consequence arise if you go to the full six-dimensional space.

3. Separation of Two-Body and Three-Body Effects

The lifetime defined by Eq. (13) for a three-body collision includes contributions from pure two-body as well as three-body interactions. This can be seen from the example sketched in Fig. 2(a), where the entire delay time is due to the two-body interaction of particles B and C. There will also be cases such as that of Fig. 2(b) where a three-body delay is due to a sequence of two-body effects, and it is often not possible to distinguish clearly between the two-body and the three-body interactions. Nevertheless, it is possible to introduce a subtraction procedure similar to that used in the original definition of the collision lifetime and thereby get rid of the type of effect shown in Fig. 2(a). For this purpose, we can subtract from the total three-body lifetime of our collision the two-body contributions that would be due to the unperturbed initial and final branches of the trajectory. In Fig. 2(b) are shown the initial trajectory P_1 and the final trajectory P_2. The net lifetime resulting from the subtraction can be written

$$Q_{\text{net}}^{(3)}(P_1,P_2)=Q^{(3)}(P_1,P_2)-\tfrac{1}{2}Q_{AB}^{(2)}(P_1)-\tfrac{1}{2}Q_{BC}^{(2)}(P_1)-\tfrac{1}{2}Q_{AC}^{(2)}(P_1)-\tfrac{1}{2}Q_{AB}^{(2)}(P_2)-\tfrac{1}{2}Q_{BC}^{(2)}(P_2)-\tfrac{1}{2}Q_{AC}^{(2)}(P_2). \quad (25)$$

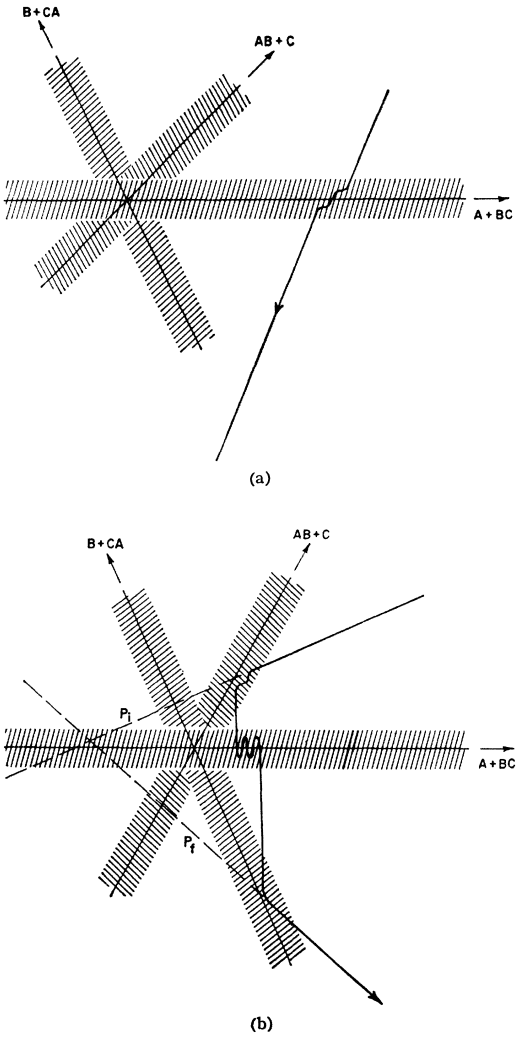

FIG. 2. (a) A two-body interaction contributing to an apparent three-body lifetime. (b) initial and final trajectories in a three-body encounter made up of several binary collisions.

In rare cases, this procedure will be seen to lead to large negative lifetimes—but trajectories involving successive collisions of the sort shown in Fig. 2(b) will be very rare in three-dimensional space. The purpose of the subtraction is rather to eliminate the adventitious two-body effect in collisions with large values of Λ^2 such as shown in Fig. 2(a), and Eq. (25) will accomplish this.

A question arises as to the treatment of collisions such as shown in Fig. 1, where the initial (or final) state is a stable two-particle pair. Clearly no subtraction is appropriate for that branch of the trajectory, and the subtraction procedure should only be applied on the side which involves three free particles.

In higher order collision lifetimes, it is again possible to subtract the effects of collisions of all lower orders in the same way.

C. QUANTUM MECHANICS

In quantal as in classical mechanics, the formulation of the lifetime matrix and the general theorems involving it require virtually no change when you go from the two-body case to the many-body case, provided only that a few of the definitions of LM are appropriately enlarged. This enlargement is conveniently done by making use of the description of many-body states as spherical waves in the $3N$-dimensional space of the relative motion of $N+1$ particles.[4] The radial coordinate in this space, ρ_N, was defined above by Eq. (3). The spherical waves are classified by a group of generalized angular momentum quantum numbers; we shall need mostly the principal one of these quantum numbers, λ as defined in GAM. As Delves[4] suggested, λ is a convenient label for three-body channels in the quantal scattering problem.

In the next section, some simple cases are examined which relate to the one just discussed classically, and it is shown how the arguments can (approximately) be translated into quantal language. Following that, the formal details of reconciling the expressions of LM and GAM are given, so that the results of LM can be applied in full generality to any nonrelativistic many-body situation.

In both of the following sections, it is necessary to refer repeatedly to the results and derivations of LM and of GAM. In order to avoid excessive repetition, familiarity with those papers must be assumed.

1. Some Special Cases: Binary Intermediates

The classical argument just given of the case where a binary intermediate participates in a three-body breakup can readily be translated into quantum mechanics. This can be done without introducing the full general formalism by using instead an argument involving wave packets. In a very simple form due to Wigner and Eisenbud,[2] this argument shows that there exists for any collision a quantal delay time strictly akin to the classical one. In the one-channel case, this quantal delay time can be shown to be identical with the collision lifetime [LM, Eqs. (15) and (21)]. In the many-channel case, the delay times form a matrix whose typical entry Δt_{ij} represents the delay in seeing a peak in the jth outgoing channel after a pulse was injected in the ith. The lifetime matrix $\mathbf{Q}$ has a different meaning in general, but its diagonal elements Q_{ii} can be shown to represent the *average* delay over all the outgoing signals after the injection of a pulse in the ith channel. In forming the average, the probability of appearance in each outgoing channel is given by the squared modulus of the appropriate element of the scattering matrix,

$$P_{ij}=|S_{ij}|^2. \tag{26}$$

It is a theorem of LM, Eq. (48), that

$$Q_{ii}=\sum_j P_{ij}\Delta t_{ij}. \tag{27}$$

This theorem applies unchanged to a case where the outgoing channels j may involve three separate particles—it is convenient in such a case to use the quantum number λ in the labeling of these outgoing states.

We can use this result in carrying over to the quantal case the classical result of the previous section on the three-body lifetimes of collisions involving an intermediate binary. The necessary modifications can conveniently be taken up one by one. First, consider the case where the principal quantal effect is in the breakup of the metastable $(BC)_m$ by quantal leakage through a potential barrier. This breakup may then occur at various times t with a probability

$$P(t,\, t+\Delta t)=(\tau_m)^{-1}\exp(-t/\tau_m)\Delta t. \tag{28}$$

The final trajectory is then seen to be characterized by the generalized angular momentum

$$|\Lambda|\cong\hbar\lambda\cong(2\mu EB)^{1/2}=2[E_m(E-E_m)]^{1/2}t. \tag{29}$$

It is now natural to consider separately the delay times for the appearance of outgoing signals in each of these channels labeled by λ; by using the theorem Eq. (26) the collision lifetime can be found by averaging over these delay times. For the moment, we assume only a single initial process, with a lifetime $Q^{(2)}$, leading to the unique metastable $(BC)_m$. The particular total three-body delay time $\Delta t^{(3)}$ associated with the appearance of an outgoing signal in a three-body channel characterized by a specific value of λ is then

$$\Delta t^{(3)}(\lambda)=Q^{(2)}+(\hbar\lambda/2E)[E_m/(E-E_m)]^{1/2}. \tag{30}$$

However, if we average over all the outgoing channels λ corresponding to this process, making use of the fact that

$$\langle t_s\rangle_{\mathrm{av}}=\int_0^\infty tP(t)dt=\tau_m \tag{31}$$

[another consequence of Eq. (26) and LM], we find

$$\begin{aligned}Q^{(3)}(E)&=\textstyle\sum_\lambda P_\lambda\Delta t^{(3)}(\lambda)\\&=Q^{(2)}(E-E_m)+\tau_m E_m/E.\end{aligned} \tag{32}$$

This is identical in form with Eq. (24), but now τ_m is a quantal (average) decay time.

We have another quantal effect in the fact that the energy of the metastable is uncertain over a narrow range of half-width

$$\Gamma_m=\hbar/2\tau_m \tag{33}$$

about E_m. As shown in LM, as corrected by footnote 3 above, this can be taken into account by introducing the energy-dependent decay lifetime of $(BC)_m$, which is half of its energy-dependent collision lifetime $Q_m(E-E_m)$. [Q_m is another two-body lifetime, entirely distinct from $Q^{(2)}$ which relates to the process that formed $(BC)_m$, while Q_m relates to its decay; it will be recalled that $\frac{1}{4}Q_m(0)=\tau_m$.] We shall write $\epsilon=E-E_m$

and assume that $Q_m(\epsilon)$ has a Breit-Wigner form of resonance about the center at E_m:

$$\tfrac{1}{2}Q_m(\epsilon)=2\hbar\Gamma(\epsilon^2+\Gamma^2)^{-1}. \quad (34)$$

Then

$$Q^{(3)}(\epsilon)=Q^{(2)}(E-E_m-\epsilon)+\tfrac{1}{2}[(E_m+\epsilon)/E]Q_m(\epsilon) \quad (35)$$

must be averaged over ϵ using the appropriate probability distribution

$$P(\epsilon)d\epsilon=(\Gamma/\pi)(\epsilon^2+\Gamma^2)^{-1}d\epsilon. \quad (36)$$

If $\Gamma\ll E_m$ and $\ll(E-E_m)$, the average over the term $\epsilon Q_m(\epsilon)$ vanishes by symmetry. As long as $Q^{(2)}$ varies slowly near $(E-E_m)$ we obtain Eq. (32) once more.

In almost any real quantal process where enough energy is present to make possible a dissociative process like $AB+C\rightarrow A+B+C$, it is improper to assume that the mechanism will go exclusively as in Eq. (14), via a single metastable intermediate $(BC)_m$. Instead, we may expect a spectrum of events varying from production of bound states of BC, through a set of metastables $(BC)_{m,j}$ of varying lifetimes $\tau_{m,j}$ to events where A, B, and C separate almost simultaneously in three-body states characterized by small values of λ. It has already been pointed out, in GAM, that the description in terms of metastables and that in terms of λ are not strictly compatible, but rather complementary. However, if the range σ of the forces is short, the lifetime is long, and the energy is large enough, the region of overlap is not very important. The criterion, deduced in GAM, can be put in the form

$$E_m(E-E_m)/E\gg\mu\sigma^2/2\tau_m^2. \quad (37)$$

This really involves two conditions: (a), $E_m\gg\mu\sigma^2/2\tau_m^2$, and (b) $E-E_m$ sufficiently large. If these are satisfied, processes involving these metastable states should be fairly well distinguishable from pure three-body processes, which should be confined to small values of λ,

$$\lambda\lesssim\hbar^{-1}(2\mu E)^{1/2}\sigma=\lambda_\sigma. \quad (38)$$

We can now consider a collision AB+C which has varying probabilities of producing all of these types of interactions: several stable bound states of AB or BC, with probabilities $P_{s,k}^{(2)}$; several metastables, with probabilities $P_{m,j}^{(2)}$, lifetimes τ_j, and energies E_j; and several pure three-body channels with $\lambda\leq\lambda_\sigma$ and probabilities $P_\lambda^{(3)}$. The corresponding delay times for the production of each of these are $\Delta t_{s,k}^{(2)}$, $\Delta t_{m,j}^{(2)}$, and $\Delta t_\lambda^{(3)}$. We must assume no significant overlapping of these processes, or the analysis in terms of metastables will be invalid; and no processes with high probability can be omitted, so that

$$\sum_{\lambda\leq\lambda_\sigma}P_\lambda^{(3)}+\sum_k P_{s,k}^{(2)}+\sum_j P_{m,j}^{(2)}\cong 1. \quad (39)$$

Now if we estimate the collision lifetime Q' of the process going from $AB+C$ to these proximate products (especially the metastables labeled by j), we find

$$Q'\cong\sum_{\lambda\leq\lambda_\sigma}P_\lambda^{(3)}\Delta t_\lambda^{(3)}+\sum_k P_{s,k}^{(2)}\Delta t_{s,k}^{(2)}+\sum_j P_{m,j}^{(2)}\Delta t_{m,j}^{(2)}. \quad (40)$$

On the other hand, if we follow the decay of the metastables, each of them contributes to the three-body products with a delay time, ultimately, of the sort

$$\Delta t_{m,j}^{(3)}=\Delta t_{m,j}^{(2)}+\tau_j E_j/E. \quad (41)$$

The complete collision lifetime Q to the ultimate products is then found to be

$$Q\cong Q'+E^{-1}\textstyle\sum_j\tau_j E_j. \quad (42)$$

2. General Formulation

This section is devoted to pointing out the modifications needed to adapt the formalism of LM to many-body collisions.

In GAM it is shown that initial and final quantal states involving $N+1$ free particles are most conveniently prescribed by the total energy E and $3N-1$ quantum numbers γ of generalized angular momentum —γ includes in particular the (integral) number λ_N such that

$$\Lambda_N^2=\hbar^2\lambda_N(\lambda_N+3N-2). \quad (43)$$

The kinetic energy of relative motion is then T_N, where

$$2\mu T_N=p_r^2+r_N^{-2}\Lambda_N^2, \quad (44)$$

so that

$$k_N^2=2\mu T_N/\hbar^2=-r_N^{3N+1}\frac{\partial}{\partial r_N}\left(r_N^{3N-1}\frac{\partial}{\partial r_N}\right)+\frac{\lambda_N(\lambda_N+3N-2)}{r_N^2}. \quad (45)$$

The eigenfunctions of the operator Λ_N^2 are generalized spherical harmonics, functions of $3N-1$ angles χ^N; their specific form will be discussed elsewhere, and is not needed here—one form is given by Delves.[4] The quantum numbers (E,γ) define the asymptotic form of the orbital part of the wave functions in the region at large r_N; for potentials vanishing more rapidly than $1/r_N^2$, the asymptotic orbital functions can be written as the product of an angular part $g_\gamma(\chi^N)$ and a radial part which is an eigenfunction of the operator of Eq. (45). For the radial part it is then convenient to write

$$_\infty\psi(r_N)\rightarrow v^{-1/2}r_N^{-(3N-1)/2}\varphi_{E,\lambda_N}(r_N), \quad (46)$$

where φ satisfies

$$\frac{d^2\varphi}{dr_N^2}-\frac{1}{r_N^2}\left(\lambda_N+\frac{3N-1}{2}\right)\left(\lambda_N+\frac{3N-3}{2}\right)\varphi+k^2\varphi=0. \quad (47)$$

Substituting

$$l'=\lambda_N+\tfrac{1}{2}(3N-3), \quad (48)$$

you can see that this is just the equation satisfied by a function $I_{l'}(kr_N)$ as used in Eq. (LM–25), which gives a recursion relation for the I's and a definition of $I_0(kr)$. However, for an odd number of particles, N is even and l' is not integral but half-integral. Then we need to define a particular half-integral case of $I_{l'}$. This can be done by using the Hankel function; for instance,

$$I_{-\frac{1}{2}}(kr) = -(\pi kr/2)^{1/2}H_0^{(2)}(kr). \tag{49}$$

In the limit as $r \to \infty$ this behaves as $i^{1/2}e^{-kr}$. As Delves[4] remarked, all the I_l's can be similarly written in terms of Hankel functions:

$$I_l(kr) = i^{2l-1}(\pi kr/2)^{1/2}H_{l+\frac{1}{2}}^{(2)}(kr). \tag{50}$$

In the limit they behave as

$$\lim_{r\to\infty} I_l(kr) = i^{3l}e^{-ikr}. \tag{51}$$

They, thus, represent purely incoming waves (I_l^* outgoing), and $v^{-1/2}I_l$ has unit inward current as $r \to \infty$. The phases are arbitrarily chosen so as most simply to follow Eq. (LM–25).

With the I_l's so defined, we can proceed to write a more general expression to replace Eq. (LM–36) as a definition of the asymptotic incoming collision function. In addition to the orbital coordinates $\mathbf{r}_N = \{r_N, \chi^N\}$, we need n_N internal coordinates $\mathbf{s}_N$ describing the internal configuration of the colliding particles ($n_N + 3N = n_1 + 3$); the collective quantum label j includes N, γ, the internal quantum numbers, and labels to identify the colliding species (e.g., $A+BC$, $B+CA$, $C+AB$, $A+B+C$). The initial phase of a collision may now be written as

$$\Phi_j = \Phi_j^- = r_N^{-(3N-1)/2} v_j^{-1/2} I_{\lambda_N+(3N-1)/2}(k_j r_N) \times g_j(\chi^N)\omega_j(\mathbf{s}_N). \tag{52}$$

The scattering matrix $\mathbf{S}$ now can include any number of incoming or outgoing partners, and the complete asymptotic wave function is still expressed by Eq. (LM–37). With appropriate interpretation of the volume elements $d\tau_r$ and $d\tau_s$, the integral expressions for $\mathbf{Q}$, (LM–38, 39), are unchanged, and the general relations between $\mathbf{S}$ and $\mathbf{Q}$, Eqs. (LM–43 through 46) follow as well.

It will be remembered that $\mathbf{Q}$ is so defined that one of its diagonal elements, say Q_{ii}, represents the average lifetime of a collision with the incoming particles uniquely in the ith channel. Even though this is a binary channel, if there is enough energy in the collision the nonvanishing S-matrix elements S_{ij} will generally include some j's corresponding to three-particle (or higher) outgoing channels. In the same way, Q_{ii} will include the effect of the many-body outgoing channels that are open even if i is a binary channel. When $\mathbf{Q}$ is diagonalized, the diagonalizing wave functions ψ_i will generally include many-body as well as binary contributions in both their incoming and outgoing parts, provided E is above the threshold for the many-body process.

3. Separation of Two-Body and Three-Body Effects

It is evident that the three-body lifetime matrix defined above includes a contribution from purely two-body interactions similar to that discussed in the classical case in connection with Fig. 2. We shall deal with this by subtracting the lifetime effects of the two-body interactions from the total three-body lifetime. However, difficulties arise because the wave functions and indices defining these different lifetimes are not the same.

We write, therefore,

$$Q_{\text{net}}^{(3)}(E;\gamma,\gamma') = Q^{(3)}(E;\gamma,\gamma') - Q_{\text{tot}}^{(2)}(E;\gamma,\gamma'), \tag{53}$$

where $Q_{\text{tot}}^{(2)}(E;\gamma,\gamma')$ is the totality of two-body lifetime contributions corresponding to the initial and final states of the three-body system. $Q_{\text{tot}}^{(2)}$ includes a contribution derived from the pair interaction AB. This can be written $Q_{AB}^{(3)}(E;\gamma,\gamma')$ to indicate that it is the three-body effect of the AB interaction alone, with C assumed not to interact. This interaction depends on the energy E_{AB}. Following Delves,[4] we can write

$$E_{AB} = E\cos^2\alpha_{AB}, \quad E_C = E\sin^2\alpha_{AB}. \tag{54}$$

We then introduce the product of wave functions adapted to this interaction in the form

$$\psi(E,\alpha_{AB},\gamma_{AB}) = \psi_{AB}(E_{AB},l_{AB},m_{AB})_\infty\psi_C(E_C,l_C,m_C), \tag{55}$$

where we write γ_{AB} for all four angular momenta. ψ_{AB} is influenced by the pair interaction, but ${}_\infty\psi_C$ is the free-particle function. We now need the expansion coefficients

$$C(\gamma\,|\,\alpha_{AB},\gamma_{AB}) \tag{56}$$

to expand the $\psi(E,\gamma)$ in terms of the product functions of Eq. (55).[5] Introducing this expansion into Eq. (LM–38), and taking advantage of the Dirac orthogonality of the functions ${}_\infty\psi_C$ with respect to E_C, we find one of the contributions to $Q_{\text{tot}}^{(2)}$ to be

$$Q_{AB}^{(3)}(E,\gamma,\gamma') = \sum_{\gamma_{AB},\gamma_{AB}'}\int_0^{\pi/2} C(\gamma\,|\,\alpha_{AB},\gamma_{AB})Q^{(2)} \times (E\cos^2\alpha_{AB}\gamma_{AB},\gamma_{AB}')C^*(\gamma'\,|\,\alpha_{AB},\gamma_{AB}')d\alpha_{AB}. \tag{57}$$

This term accounts for the contribution of the initial, incoming wave functions of the total three-body process; we must also consider the outgoing wave functions, which are connected with the incoming ones by the three-body scattering matrix $\mathbf{S}^{(3)}$. Thus we need not only $\mathbf{Q}_{AB}^{(3)}$ but its transform $\mathbf{S}^{(3)}\mathbf{Q}_{AB}^{(3)}\mathbf{S}^{(3)}\dagger$. $\mathbf{Q}_{\text{tot}}^{(2)}$ then includes $\frac{1}{2}\mathbf{Q}_{AB}^{(3)} + \frac{1}{2}\mathbf{S}^{(3)}\mathbf{Q}_{AB}^{(3)}\mathbf{S}^{(3)}\dagger$ plus similar terms for the interactions BC and AC.

[5] See Delves, reference 4, for the expansion coefficients.

Similar subtractions can be introduced in the higher order collision lifetimes.

4. The Complete Lifetime Matrix

In processes where a bound state participates, as in the reaction $AB+C \rightarrow A+B+C$, the formulation of Q that was used above does not require any subtraction for the bound state AB because the collision $AB+C$ was treated as a purely two-body event. However, it is possible to take an alternative viewpoint in which the bound state AB is treated as the limiting case of a long-lived metastable. To see how this can come about, consider a metastable with a long lifetime, which is describable near its maximum at E_m by the function

$$Q_m(E)=2\hbar\Gamma_m[(E-E_m)^2+\Gamma_m^2]^{-1}, \qquad (58)$$

where Γ_m is the half-width of the resonance. A true bound state can be described in the same way provided we let $\Gamma_m \rightarrow 0$, turning $Q_m(E)$ into a δ function. Thus, bound states can be treated in the same way as the metastables and the continuum—and we note that even bound states which are not free to dissociate spontaneously usually have finite widths Γ_m due to radiation or other interactions with the environment. Thus, the bound states can be treated formally in the same way as the continuum. If this is done, we can treat the gross $Q^{(3)}$ for the collision $AB+C$ as involving an infinite lifetime due to the δ-function lifetime $Q_{AB}(E_{AB})$; when this δ function is subtracted away to obtain $Q_{\text{net}}^{(3)}$ we end up where we were before. However, this viewpoint introduces a greater formal unity into the picture.

As a matter of fact, this way of treating bound states on a par with the unbound ones suggests that it may be useful to focus our attention not quite so much on the number of free particles entering into the collision as on the number of particles in the collision complex. Thus, we can consider as contributing parts of a single lifetime matrix $\mathbf{Q}_{ABC}(E)$ all the combinations which involve an excess (or deficiency) of population near the origin of a diagram like Fig. 1 or 2. These include: bound states of ABC, with $\mathbf{Q}_{ABC}(E)$ as a δ function or a function of the form of Eq. (58); two-body lifetimes $\mathbf{Q}^{(2)}$ for collisions like $AB+C \rightarrow AB+C$ or $AB+C \rightarrow A+BC$; and net three-body lifetimes $\mathbf{Q}_{\text{net}}^{(3)}$ for events like $AB+C \rightarrow A+B+C$ or $A+B+C \rightarrow A+B+C$. Of course, the energy E must then be the total energy of the three-body system, measured from some convenient origin (for instance, the ground state of ABC, or the free particles $A+B+C$ at rest), and E must run through the whole spectrum, including negative as well as positive energy states.

The trace of a complete lifetime matrix such as $\mathbf{Q}_{ABC}(E)$, $\mathrm{Tr}\mathbf{Q}_{ABC}$, is of fundamental importance. I shall show elsewhere[6] that the complete partition function for the molecular system ABC (including transient collision complexes) is the product of the usual translational partition function and an internal one

$$Z_{ABC}^{(\text{int})}=h^{-1}\int_{E_0}^{\infty} e^{-E/kT}\,\mathrm{Tr}\mathbf{Q}_{ABC}(E)dE. \qquad (59)$$

For bound and metastable states, with a form like Eq. (58), this reduces approximately to the familiar form,

$$Z_{ABC}^{(\text{int})}=\sum_i \omega_i e^{-E_i/kT}. \qquad (60)$$

The partition function $Z_{ABC}^{(\text{int})}$ of Eq. (59) has a central role in the development of an exact cluster expansion for the thermodynamic properties of real gases.

[6] F. T. Smith, J. Chem. Phys. 38, 1304 (1963).