Connection between the maximal entropy and the scattering theoretic analyses of collision processes

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(Received 7 June 1977)

The information-theoretic maximal-entropy procedure for the analysis of collision processes is derived as a consequence of the dynamics, be they quantal or classical. The method centers attention on the minimal number of operators (the "dynamic constraints") whose expectation values are both necessary and sufficient to completely characterize the collision dynamics. For a given Hamiltonian and initial state, the constraints required to obtain an exact solution of the equations of motion are determined by a purely algebraic procedure. It is furthermore found possible to derive equations of motion for the conjugate Lagrange parameters. Immediate applications are noted, e.g., a family of similar reactions is shown to have a common set of dynamic constraints and simple illustrative applications are provided. The determination of the scattering matrix is discussed, with examples. The general formalism consists in solving the scattering problem in two stages. The first is purely algebraic. At the end of this stage one obtains the functional form of, say, the scattering matrix or of the density matrix after the collision expressed in terms of parameters whose number equals the number of dynamic constraints. The end result of this algebraic stage suffices to analyze the scattering pattern for any initial state. The second stage is the predictive procedure. Explicit coupled first-order nonlinear differential equations are obtained for the parameters.

I. INTRODUCTION

There is a large body of experimental results[1,2] for collisions of composite projectiles (be they nuclei or molecules) showing, for example, considerable specificity in the population of the accessible final states. Statistical theories are thus not sufficient to account for the data, yet the coupling is far too strong for simple perturbation theory to apply. Close-coupling computational schemes are required and when they can be carried out their results are typically in good accord with experiment, both in general qualitative trends and detailed quantative conclusions. Such computations are, however, not easy to implement nor is there a simple interpretation of the final results, particularly when only a partial resolution of the final states is provided by the experiment. It is thus of some interest to develop a scheme whereby the experimental or computational results can be analyzed, correlated, and compacted.

On the basis of information-theoretic (maximal-entropy[3-8]) considerations, it was suggested[9] that while the final phase space is not uniformly filled, the constraints leading to the nonstatistical final-state distribution are often simple and can be determined directly from the data. Many inelastic and rearrangement collision processes in both molecular[9] and nuclear[10] physics have already been analyzed in this fashion. Specifically, one assumes that the density operator[11] ρ, for the system after the (single) collision, can be expressed as

$$\rho = \exp\left(-\sum_{r=0}\lambda_r A_r\right), \tag{1.1}$$

where A_r's are operators (with $A_0 = I$, the identity operator) and the λ_r's are numerical coefficients. The operators A_r (called the "constraints") and the coefficients λ_r are determined either from experimental results or from some theoretical considerations. Thus far, information theoretic arguments have played a central role in motivating our choice of the functional form Eq. (1.1), and in subsequent manipulations. The applications[9] of Eq. (1.1) to diverse aspects of molecular-collision processes have stimulated other derivations[12] of limiting forms of Eq. (1.1). These were often based on a distorted-wave approximation and invoked additional simplifications unique to the molecular problem. Recently however it was noted that the representation (1.1) could be usefully employed[10] to analyze experimental results for both inelastic (Coulomb excitation[13]) and rearrangement (e.g., α transfer[1,14]) nuclear collisions. Moreover, there is computational evidence[15] that the maximal-entropy approach is useful for describing the evolution of the system during (and not only after) the collision.

The purpose of the present study is to document the validity and utility of the functional form, Eqs. (1.1), as an exact solution of the equations of motion, be they quantal or classical, for a collisional

process. We shall, for convenience, adopt a time-dependent formalism and discuss the existence, construction, and properties of an evolution matrix $\underline{G}$ such that at any time t during the collision

$$\lambda_r(t) = \sum_s G_{rs}\lambda_s(-\infty) \tag{1.2}$$

and

$$\mathrm{Tr}[\rho(t)A_r] = \langle A_r\rangle(t) = \sum_s \langle A_s\rangle(-\infty)G^{-1}_{sr}. \tag{1.3}$$

The applications we shall consider are to processes, where the interaction is explicitly time dependent (e.g., a collision where the relative motion is treated in a classical fashion such as, say, Coulomb excitation[13] where the colliding nuclei move along a Rutherford trajectory). The formalism can however be employed also in the context of time-independent scattering theory as will be explicitly demonstrated in a separate publication.

The central theme of Sec. II is that an initial state, chosen to maximize the entropy (subject to the constraints of the preparation procedure), remains a state of maximal entropy throughout the collision. It is thus possible to construct a set of operators, closed under commutation with the Hamiltonian, such that the maximal-entropy density matrix specified by their expectation values is an exact solution of the equation of motion. The algebraic definition of the constraints as used here retains the ties with (equilibrium) thermodynamics, where the constraints employed are those operators that commute with the Hamiltonian.[16] A set of constraints of particular importance is the so-called "dynamic constraints." These form a Lie algebra.[17] The term similar reactions is given a precise definition and it is shown that similar reactions have a common set of dynamic constraints.

The formalism is applied to the two simplest examples of vibrational and rotational excitation in Sec. III. Many of our results for the forced harmonic-oscillator problem are well known[18-22] and we have chosen this example so as to illustrate the formalism in a familiar context.

The formal theory is presented in Sec. IV, where the concepts of the dynamical group and the group parameters are discussed. With these developments it is possible to obtain a universal solution for the $\underline{G}$ matrix which is valid for all reactions of the same family. Different members of a family of similar reactions differ only in the values of the group parameters that are present as coefficients in the expression for $\underline{G}$.

The Lie algebraic implications of the formalism are discussed in Sec. V. The usual formulations of scattering theory seek a representation of the dynamical group in a Hilbert space of state vectors.[23-25] The simplifications achieved by the present formalism are due to the fact that it obtains a representation in the space of relevant operators. Even for the usual formulations the concept of the representation of a Lie group affords a very practical tool enabling us to compute the elements of the scattering matrix as analytic functions of group parameters whose number is equal to the number of dynamic constraints and which satisfy (nonlinear) equations of motion that are often readily solvable. A nontrivial example is provided in Appendix B.

Several applications of the formalism to the derivation of closed-form results for realistic Hamiltonians of both inelastic and rearrangement collisions are in preparation for publication. Other work in progress includes the analysis of experimental results aimed at identifying the dynamical algebra from the observed constraints. This is being attempted for several families of similar collisions, both molecular and nuclear.

II. CONSTRUCTION OF THE FORMALISM

To characterize a scattering experiment one needs to construct the initial state and then solve the equation of motion. In this section we consider both problems. The initial state is selected as the (unique) state of maximal entropy[3-8] subject to the condition that it correctly yields the expectation values of the different initial observables. Any other density operator which also yields the same expectation values has a lower entropy. Since[27] entropy is a constant of the motion [cf. Eq. (2.11) below], an initial state of maximal entropy necessarily remains a state of maximal entropy throughout the collision. While this result is assured as long as the time evolution is unitary, it falls short of a "construction" theorem. All that it does state is that the density operator of the system is one of maximal entropy subject to the expectation values of those operators that have evolved (in the Heisenberg picture) from the operators required to specify the initial state. Our second purpose is to determine these operators explicitly, by an algebraic procedure. Given the Hamiltonian and the set of constraints that characterize the initial precollision density operator we determine a set of constraints that characterize the density operator throughout the collision. The density operator of maximal entropy subject to these constraints is an exact solution of the equation of motion.

In addition to the procedure for the algebraic identification of the constraints it is shown that the value of the Lagrange parameters at any time t can be determined. The solution of the equation of motion is thereby replaced by solving a set of

coupled, linear, differential equations whose number is equal to the number of constraints.

The procedure of this section has the advantage that it generates the density operator (during and after the collision) for the initial state of interest. The more formal approach of Sec. IV, which determines the evolution operator and hence applies to any initial state, also shows that the number of coupled equations of motion that need be solved equals the number of dynamic constraints, irrespective of the specification of the initial state.

A. Procedure of maximal entropy

The initial state in a collision is prepared by the experimentalist. The data available are the magnitudes of the expectation values of the different operators. Collision experiments with composite projectiles will often achieve only a partial selection of the initial state.[2(b),28] This need not however be the case and one can also consider the limiting case of a dispersion-free preparation procedure [see Eq. (2.8) below and the example in Sec. IIIC)]. This will typically be the case in the analysis (e.g., Ref. 15) of computational (close-coupling) studies.

The (information theoretic) entropy of the density operator ρ is[26] (in "natural" units)

$$S = -\mathrm{Tr}\{\rho \ln \rho\}. \tag{2.1}$$

The preparation of the initial state ρ consists in the specification of the magnitudes of the expectation values of a set of (not necessarily commuting, but linearly independent) operators,

$$\langle A_r \rangle = \mathrm{Tr}\{\rho A_r\}, \quad r = 0, 1, 2, \ldots . \tag{2.2}$$

We take A_0 to be the identity operator so that ρ is normalized $\langle A_0 \rangle = 1$.

The initial-density operator is selected to be of maximal entropy subject to the conditions, Eq. (2.2). It is constrained to be consistent with the results of the preparation procedure, but otherwise it spans the largest possible volume in phase space.[29] The resulting expression for ρ is well known[4-8]

$$\rho = \exp\left(-\lambda_0 - \sum_{r=1} \lambda_r A_r\right). \tag{2.3}$$

The magnitudes of the (Lagrange) parameters λ_r are determined by the condition that ρ is normalized

$$\mathrm{Tr}(\rho) = 1, \tag{2.4}$$

and accounts for the magnitude of the other expectation values [i.e., that Eq. (2.2) holds for $r = 1, 2, \ldots$]. The only condition on the operators is that there exists some set of numbers $\lambda_0, \lambda_1, \lambda_2, \ldots$, for which the trace in Eq. (2.4) is finite.[30] An explicit example (Sec. IIIB) shows that when two operators fail to commute, the condition (2.4) insures that the product of their dispersions exceeds the bound set by the uncertainty principle.

In practice it may well be that one (or more) of the Lagrange parameters, say λ_q, is identically zero. This implies that even when the magnitude of $\langle A_q \rangle$ is not included as a constraint during the maximization of S, the resulting density operator would predict the correct magnitude of the expectation value $\langle A_q \rangle$. From now on we limit our considerations to the set of $n+1$ operators A_r, $r = 0, 1, \ldots, n$, which are found necessary to specify the initial-state (i.e., for which λ_r is nonvanishing. Since the operators are linearly independent the Lagrange parameters are unique[8]).

The rationale for selecting the density operator of maximal entropy to describe the state of the system following a preparation procedure has been discussed in the literature.[3-8] The information-theoretic motivation is clear cut. Among all density operators consistent with the constraints the density operator of maximal entropy is the most chaotic: It corresponds to the largest possible volume in phase space[29]; it has the lowest information content; its eigenvalues are more uniform,[29] and are the most probable distribution.[9(d)] In addition, it does yield the conventional results[26] when applied to a procedure that measures just one operator, say M. Introducing the spectral resolution of M,

$$M = \sum_i m_i P_i, \tag{2.5}$$

where the P_i's are projection operators, Eq. (2.3) gives

$$\rho = e^{-\lambda_0 - \lambda M} = \sum_i e^{-\lambda_0 - \lambda m_i} P_i = \sum_i P_i \rho P_i. \tag{2.6}$$

Similarly, consider a procedure that measures the expectation values of a set $\{P_i\}$ of projection operators $P_i P_j = P_i \delta_{ij}$. Introducing $Q_j = I - P_j$, the complementary projection to P_j, $P_i Q_j = (1 - \delta_{ij}) P_i$, we obtain from Eq. (2.3)

$$\rho = \exp\left(-\lambda_0 - \sum_i \lambda_i P_i\right),$$

and since the projectors commute

$$\rho = e^{-\lambda_0} \prod_i (Q_i + e^{-\lambda_i} P_i) = e^{-\lambda_0} \sum_i e^{-\lambda_i} P_i. \tag{2.7}$$

Determining λ_0 by Eq. (2.4) and λ_i by the condition that $\mathrm{Tr}(\rho P_i)$ has its measured value

$$\rho = \sum_i \mathrm{Tr}(\rho P_i) P_i = \sum_i P_i \rho P_i. \tag{2.8}$$

The preparation of a pure state ($\mathrm{Tr}(\rho P_i) = \delta_{ij}$) is a special limiting case, but less than perfect state selection can also be described by the procedure of maximal entropy.

B. Time evolution

In the Schrödinger picture the time evolution is described by a unitary evolution operator $U(t, t_0)$. In particular, the density operator at time t is given by

$$\rho(t) = U(t, t_0)\rho(t_0)U^\dagger(t, t_0). \tag{2.9}$$

Then, since $\ln x$ has a convergent-power-series expansion for $0 < x < 2$, and invoking the unitarity of the evolution operator

$$\begin{aligned}\ln[\rho(t)] &= \ln[U(t, t_0)\rho(t_0)U^\dagger(t, t_0)] \\ &= U(t, t_0)\ln[\rho(t_0)]U^\dagger(t, t_0).\end{aligned} \tag{2.10}$$

The result, Eq. (2.10), serves to prove that the entropy is time independent,[31] (from now on we supress the argument of the evolution operator),

$$\begin{aligned}S &= -\mathrm{Tr}[\rho(t)\ln\rho(t)] \\ &= -\mathrm{Tr}[U\rho(t_0)U^\dagger U \ln\rho(t_0)U^\dagger] \\ &= -\mathrm{Tr}[U^\dagger U\rho(t_0)\ln\rho(t_0)] \\ &= -\mathrm{Tr}[\rho(t_0)\ln\rho(t_0)].\end{aligned} \tag{2.11}$$

Among all density operators consistent with the magnitude of the initial $n+1$ expectation values, the one of maximal entropy will remain of maximal entropy through the time evolution. An alternative and more constructive route is to examine the time evolution of the initial-density operator,[32] cf. Eq. (2.3),

$$-\ln\rho(t_0) = \sum_{r=0}^{n} \lambda_r(t_0) A_r. \tag{2.12}$$

Using Eq. (2.10)

$$-\ln\rho(t) = \sum_{r=0}^{n} \lambda_r(t_0) U A_r U^\dagger. \tag{2.13}$$

The density operator at time t is seen to have explicitly the form of a density operator of maximal entropy subject to the magnitude of the $n+1$ expectation values $\mathrm{Tr}[\rho(t)UA_rU^\dagger]$. These expectation values are however known, for on using[9]

$$\mathrm{Tr}[\rho(t)UA_rU^\dagger] = \mathrm{Tr}[U^\dagger\rho(t)UA_r] = \mathrm{Tr}[\rho(t_0)A_r], \tag{2.14}$$

and the $n+1$ expectation values $\mathrm{Tr}[\rho(t_0)A_r]$ are precisely those that were used to constrain the initial state, cf. Eq. (2.12).

Solving explicitly for the density operator at the time t has thus been shown equivalent to determining explicitly the n operators of the type $U(t, t_0)A_rU^\dagger(t, t_0)$, $r = 1, 2, \ldots, n$. In particular, the constraints required to specify the density operator after the collision are then n operators of the form $SA_rS^\dagger$ (where S is the scattering operator) plus the identity.

C. Explicit determination of the constraints

The explicit constraints that are required to specify the density operator at the time t are all those (linearly independent) operators A_r, $r = 0, 1, \ldots, m$, $m \geq n$, that are present in the expansion of the surprisal, $-\ln\rho(t)$:

$$-\ln\rho(t) = \sum_{r=0}^{m} \lambda_r(t) A_r. \tag{2.15}$$

Here $\lambda_r(t_0) = 0$ for $n < r \leq m$ and the first $n+1$ operators are necessarily present if Eq. (2.15) is also to hold for the initial state (i.e., as $t \to t_0$).

Equating the explicit, Eq. (2.15), and implicit, Eq. (2.13), expansions of the surprisal,

$$\sum_{r=0}^{m} \lambda_r(t) A_r = \sum_{s=0}^{n} \lambda_s(t_0) U A_s U^\dagger. \tag{2.16}$$

The operators A_r are linearly independent and the expansion, Eq. (2.15), need be valid for any time t during the collision. Hence one can equate the coefficients of A_r on both sides of Eq. (2.16). It follows that Eq. (2.15) obtains if and only if there exists a (time-dependent) matrix $\underline{G}$ whose elements are defined by

$$UA_sU^\dagger = \sum_{r=0}^{m} A_r G_{rs}. \tag{2.17}$$

The "if" part is demonstrated by substituting Eq. (2.17) in Eq. (2.16) whence one obtains

$$\lambda_r(t) = \sum_s G_{rs}\lambda_s(t_0). \tag{2.18}$$

The "only if" part requires taking Eq. (2.16) to hold at $m+1$ different times and solving for the A_r's,

$$U^\dagger A_r U = \sum_{s=0}^{m} (\underline{G}^{-1})_{sr} A_s. \tag{2.19}$$

An alternative and more practical way to state the condition, Eq. (2.17), is obtained by taking the time derivative of both sides. Using the time-dependent Schrödinger equation $i\hbar\partial U/\partial t = HU$, and noting that $U(t_0, t_0) = I$, we obtain

$$[H, A_s] = \sum_{r=0}^{m} A_r \alpha_{rs}, \tag{2.20}$$

where $\alpha_{rs} = i\hbar\partial G_{rs}/\partial t$ evaluated at $t = t_0$.

The set of $m+1$ constraints that characterizes the density operator at any time t is a set of operators closed under commutation with the Hamiltonian.

Given the set $\{A_r\}$ of $n+1$ operators that characterizes the initial state [i.e., that appear in the expansion of $-\ln\rho(t_0)$] one forms all operators of the type $[H,A_r]$, say, equal to A_q. If the n operators A_q are linear combinations of the $n+1$ operators of the initial set, it is already closed. If not, the original set need be augmented by the new operators and commutators of the type $[H,[H,A_r]] = [H,A_q]$ need be examined, etc., until the resulting set is closed. Those operators which have been employed to augment the original set are taken to appear in $-\ln\rho(t)$ with a Lagrange parameter that vanishes for $t=t_0$. For operators defined in a finite-dimensional Hilbert space a finite set of constraints is guaranteed to exist. For operators defined in an infinite-dimensional Hilbert space this may but need not be the case. It is then necessary to appeal to the Fredholm-Schmidt theorem[33] which guarantees that the surprisal $-\ln\rho$ [which has a finite trace, $S=-\mathrm{Tr}(\rho\ln\rho)$] can be approximated to any required accuracy by a finite number of terms.

The physical interpretation of the "closure" condition, Eq. (2.20), is readily seen by taking the expectation value [over $\rho(t)$] of both sides.

$$\frac{\partial\langle A_r\rangle(t)}{\partial t} = \mathrm{Tr}\left\{A_r\frac{\partial\rho(t)}{\partial t}\right\}$$

$$= (i\hbar)^{-1}\,\mathrm{Tr}\{A_r[H,\rho]\}$$

$$= -(i\hbar)^{-1}\,\mathrm{Tr}\{\rho(t)[H,A_r]\}$$

$$= -(i\hbar)^{-1}\sum_s \alpha_{sr}\langle A_s\rangle(t), \qquad (2.21)$$

or in matrix notation

$$\frac{\partial\langle\underline{A}\rangle(t)}{\partial t} = -(i\hbar)^{-1}\langle\underline{A}\rangle(t)\cdot\underline{\alpha}\ . \qquad (2.22)$$

Here $\langle\underline{A}\rangle(t)$ is the row vector whose components are the $m+1$ expectation values $\langle A_r\rangle(t)\equiv\mathrm{Tr}\{A_r\rho(t)\}$. The rate of change of any constraint is a linear combination of the instantaneous expectation values of the other constraints. Given $\langle\underline{A}\rangle(t_0)$, the linear differential equation (2.22) uniquely determines $\langle\underline{A}\rangle(t)$. The explicit solution for $\langle\underline{A}\rangle(t)$ is discussed in Sec. V.

The result Eq. (2.22) is valid for any initial density operator but by itself is of limited utility. It determines the expectation values of the constraints but to determine the expectation value of an arbitrary operator which is not a member of the closed set one still requires the density matrix. It is the procedure of maximal entropy which enables us to use the closed set of constraints for that purpose.

D. Constraints in the classical limit

To transcribe the results to classical mechanics it is necessary to replace the commutator bracket by a Poisson bracket according to the well-known correspondence

$$(i\hbar)^{-1}[\ ,\ ] \to \{\ ,\ \}. \qquad (2.23)$$

Now ρ is the density in phase space, satisfying the classical Liouville equation $\partial\rho/\partial t=\{H,\rho\}$ or $\partial\ln\rho/\partial t=\{H,\ln\rho\}$ and the A_r's are functions of dynamic variables which are closed under the operation $\{H,\ \}$. Using Eq. (2.23) in Eq. (2.20) we have

$$\{H,A_r\} = (i\hbar)^{-1}\sum_s \alpha_{sr}A_s. \qquad (2.24)$$

Hence, when we make the correspondnece Eq. (2.23) in Eq. (2.21) we find that the equation of motion for the constraints or for the Lagrange parameters, Eqs. (2.22) or (2.29), have precisely the same form in classical as in quantum mechanics. The functional form for $\rho(t)$, Eq. (2.15), and the associated equations of motion remain unchanged in the classical limit.

The real simplification provided by classical mechanics is that the classical ρ is directly the probability density function in phase space.[34] In contrast, the quantal ρ is still an operator whose (diagonal) matrix elements need be evaluated to compare with the experimental probabilities.

E. $\underline{G}$ (or "super evolution") matrix

The $\underline{G}$ matrix[35] defined by Eq. (2.17) propagates the Lagrange parameters in time, cf. Eq. (2.18). Similarly, by taking the expectation value of both sides of Eq. (2.17)

$$\mathrm{Tr}\{\rho(t)UA_sU^\dagger\} = \mathrm{Tr}\{U^\dagger\rho(t)UA_s\}$$

$$= \mathrm{Tr}\{\rho(t_0)A_s\}$$

$$= \sum_r G_{rs}\,\mathrm{Tr}\{\rho(t)A_r\} \qquad (2.25)$$

or

$$\langle A_s\rangle(t_0) = \sum_r G_{rs}\langle A_r\rangle(t). \qquad (2.26)$$

In matrix notation

$$\langle\underline{A}\rangle(t) = \langle\underline{A}\rangle(t_0)\cdot\underline{G}^{-1}. \qquad (2.27)$$

The Lagrange parameters, cf. Eq. (2.18) and the constraints, cf. Eq. (2.26) or (2.27), evolve with time in an opposite, contragradient manner.

The differential equation, Eq. (2.22), implies that $\underline{G}$ [or more properly, $\underline{G}(t,t_0)$] satisfies the differential equation

$$\frac{i\hbar\partial \underline{G}}{\partial t} = \underline{\alpha}\,\underline{G}, \tag{2.28}$$

with the boundary condition that as $t \to t_0$, $\underline{G} \to \underline{I}$. Instead of solving Eq. (2.21) or the corresponding equation,

$$\frac{\partial \lambda_r(t)}{\partial t} = \sum_s \alpha_{rs}\lambda_s(t), \tag{2.29}$$

for the Lagrange parameters one can solve for $\underline{G}$ and determine the time evolution using Eqs. (2.18) or (2.27). (In Sec. V F we shall show that when $\underline{G}$ is known then $\underline{G}^{-1}$ is immediately available without the need for the usual procedure of matrix inversion.) The advantage of determining $\underline{G}$ first is, as is evident from Eq. (2.28) and its boundary condition, that the same matrix $\underline{G}$ applies irrespective of the magnitude of the initial constraints. Any initial state, that can be characterized by the $m+1$ constraints of the closed set, evolves under the same $\underline{G}$ matrix. For any set of constraints it is only necessary to compute the $\underline{G}$ matrix once and for all and efficient methods for doing this are discussed in Sec. V. The specific data of a particular initial state enters only through the linear transformations, Eqs. (2.18) and (2.26). The expectation values of the constraints at the time t are linear combinations of their initial values and similarly for the Lagrange parameters.

Given a matrix $\underline{G}$, we see from Eqs. (2.18) and (2.26) that the row r of the matrix specifies which initial Lagrange parameters contribute to $\lambda_r(t)$, while the column s specifies which operators at time t have evolved out of the initial operator A_s. It is therefore of considerable interest to be able to identify those elements of $\underline{G}$ that are identically zero. We shall see in Sec. V (and in the examples) that this is indeed possible and that there are many such elements. A trivial example is that, for $r \neq 0$, $G_{r0} = 0$. The proof is immediate, by taking, as usual, A_0 to be the identity operator. Since $UIU^\dagger = I$ and $U^\dagger I U = I$, the required conclusion follows.

F. Transformations of the constraints

It is sometimes convenient to replace one set $\{A_r\}$ of constraints by another, equivalent set, say $\{C_r\}$. It should then be possible to represent any constraint A_s [and hence $\ln\rho(t)$] as a linear combination of the C_r's and vice versa. Thus, if the two sets are equivalent there exists a square nonsingular matrix $\underline{W}$ such that

$$C_r = \sum_s W_{sr}A_s; \quad A_s = \sum_r W^{-1}_{rs}C_r. \tag{2.30}$$

Let the $\underline{G}$ matrix for the equivalent set be denoted by $\underline{\overline{G}}$, i.e.,

$$UC_rU^\dagger = \sum_s \overline{G}_{sr}C_s.$$

Substituting for C_r its expansion in terms of the first set one readily verifies that

$$\underline{\overline{G}} = \underline{W}^{-1}\underline{G}\,\underline{W}. \tag{2.31}$$

A transformation to an equivalent set of constraints implies a similarity transformation of the $\underline{G}$ matrix. Depending on the Hamiltonian (the precise conditions are formulated in Secs. V F and V G) it may indeed be possible to choose a set of constraints such that its $\underline{G}$ matrix is particularly simple.

The density operator should of course be invariant under any equivalent change in the constraints. Denoting the Lagrange parameters conjugate to the C_r's as γ_r's,

$$\ln\rho(t) = -\sum_{r=0}\gamma_r(t)C_r \equiv -\sum_{r=0}\lambda_r(t)A_r. \tag{2.32}$$

Using Eq. (2.30), the equivalence, Eq. (2.32), implies

$$\gamma_r = \sum_s W^{-1}_{rs}\lambda_s; \quad \lambda_s = \sum_r W_{sr}\gamma_r. \tag{2.33}$$

Comparing Eqs. (2.30) and (2.33) we see that the Lagrange parameters transform in an opposite (contragradient) manner to the constraints. (The same was true for transformations induced by time evolution.)

G. Dynamical algebra

A key observation in the application[9,10] of the representation Eq. (1.1) for ρ to the analysis of experimental results is that the same set of constraints is valid for all the different reactions which proceed via a similar mechanism. We now derive the corresponding theoretical result.

The set of operators A_r that serve as constraints is invariant under commutation with $H(t)$,

$$[H(t), A_r] = \sum_s A_s\alpha_{sr}(t). \tag{2.34}$$

The time dependence of the Hamiltonian is indicated explicitly in Eq. (2.34) since this dependence can be different for similar problems. As a simple example, say the time dependence stems from a classical treatment of the relative motion. Then trajectories with different impact parameters will lead to different time-dependent Hamiltonians. In the more general case, when we are working explicitly in the interaction picture (Secs. IV and V), so that the $H(t)$ is really $V_I(t)$, different level spacings in H_0 will lead to different potentials, etc. We now define a set of "similar" processes by the condition that their Hamiltonians are all of the

form

$$H(t)=\sum_{n=1} h_n(t)H_n. \tag{2.35}$$

Here the operators H_n are time independent and different collisions differ only in the (time-dependent) functions $h_n(t)$.

The same set of constraints A_r obtains for all the similar collisions if it is closed under the commutation with each and every one of the "Hamiltonians" H_n,

$$[H_n,A_r]=\sum_s d_{sr}(H_n)A_s, \quad n=1,\ldots . \tag{2.36}$$

Here $d_{sr}(H_n)$ is a time-independent coefficient which depends on the indices s and r and differs for different operators H_n. It is readily verified that Eq. (2.36) [and Eq. (2.35)] imply that Eq. (2.34) obtains for all the similar reactions

$$\begin{aligned}[H(t),A_r]&=\sum_n h_n(t)[H_n,A_r]\\ &=\sum_n\sum_s h_n(t)d_{sr}(H_n)A_s\\ &=\sum_s A_s\Big(\sum_n h_n(t)d_{sr}(H_n)\Big).\end{aligned} \tag{2.37}$$

Thus,

$$\alpha_{sr}(t)=\sum_n h_n(t)d_{sr}(H_n). \tag{2.38}$$

When the condition (2.36) is obtained, the maximal-entropy solution for all the similar collisions will be characterized by the very same set of constraints. The different collisions will differ only in the values of the Lagrange parameters, as their time evolution is determined by the matrix $\alpha(t)$ [cf. Eq. (2.19)], which does depend [via the time dependence of the $h_n(t)$'s, cf. Eq. (2.38)] on the details of the particular process.

It will turn out to be very convenient to cast the discussion in a more general form as follows. The set of operators $\{H_n\}$ that appear in the resolution of the Hamiltonian [cf. Eq. (2.35)] need not be necessarily closed under commutation of the operators among themselves. That is, if H_n and H_m are members of the set, it may not be possible to express $[H_m,H_n]$ as a linear combination of operators in the set. Should this be the case, we augment the set by the addition of the operator $H_l=[H_m,H_n]$ even though for the Hamiltonian $H(t)$ in Eq. (2.35) $h_l(t)\equiv 0$. One proceeds to augment the original set until a minimal set of operators that is closed under commutation of its members is obtained. For any two operators H_n, H_m of this set

$$[H_n,H_m]=\sum_r C^r_{nm}H_r. \tag{2.39}$$

Such a minimal set is known as the Lie algebra[17] generated by the operators that appear in the Hamiltonian. The coefficients C^r_{nm} are known as the "structure constants" of the algebra.

We shall refer to the Lie algebra defined above as "the dynamical algebra" and to the operators H_n as the elements of the algebra. These elements will turn out to be the building blocks of the formalism.

We now show that the set of "common constraints," introduced in Eq. (2.36) as the set closed under commutation with every operator in the Hamiltonian is necessarily also closed under commutation with every element of the dynamic algebra. The proof is based on the Jacobi identity

$$[[A,B],C]+[[B,C],A]+[[C,A],B]=0. \tag{2.40}$$

Consider an element of the dynamical algebra, say $H_l=[H_m,H_n]$ which is not an operator that appears in the Hamiltonian [i.e., $h_l(t)\equiv 0$ in Eq. (2.35)]. Therefore the case $n=l$ was not included in the definition, Eq. (2.36), of the common constraints. However

$$\begin{aligned}[[H_m,H_n],A_r]&=[[H_m,A_r],H_n]-[[H_n,A_r],H_m]\\ &=\sum_s\{d_{sr}(H_m)[A_s,H_n]-d_{sr}(H_n)[A_s,H_m]\}\\ &=\sum_s\sum_t\{d_{sr}(H_n)d_{ts}(H_m)\\ &\qquad -d_{sr}(H_m)d_{ts}(H_n)\}A_t\end{aligned} \tag{2.41}$$

or, with $H_l=[H_m,H_n]$,

$$[H_l,A_r]=\sum_t d_{tr}(H_l)A_t \tag{2.41'}$$

with

$$d_{tr}(H_l)=\sum_s\{d_{ts}(H_m)d_{sr}(H_n)-d_{ts}(H_n)d_{sr}(H_m)\}, \tag{2.42}$$

In Sec. V C we shall come to recognize Eq. (2.42) as implying that the constraints provide a basis for the representation of the dynamic algebra.

Similar collision processes have thus been characterized as having a common dynamic algebra and hence as having a common set of dynamic constraints.

The above result is simple but not trivial. Different Hamiltonians, composed of different operators, can generate the same dynamical algebra and hence give rise to a common set of constraints. For example, the operator H_l assumed above to be absent from the Hamiltonian [i.e., $h_l(t)\equiv 0$, cf. Eq. (2.35)] may be present in some other Hamiltonian $H'(t)$ [i.e., $h'_l(t)\neq 0$]. Yet, $H(t)$ and $H'(t)$ should rightly be considered members of the same family.

H. Dynamic constraints

The constraints have been defined as a set of operators that is closed under commutation with each one of the operators H_n that are the elements of the dynamical algebra. There is one set of operators (the "dynamic constraints") that will inherently satisfy this condition, i.e., the set of operators that is, itself, the dynamical algebra [cf. the definition, Eq. (2.39), of this set]. It follows that the set of constraints can include all the operators that are the elements of the dynamical algebra but may include additional operators.

The origin of those, sometimes present, additional constraints is readily traced to those constraints that were required to specify the initial state $\rho(t_0)$, Eq. (2.12). If the initial state can be fully specified using only (some or all) dynamic constraints then these suffice throughout the collision. If one (or more) additional operators are required to specify $\rho(t_0)$ then the set of constraints will include additional operators which are not dynamical constraints.

Let the set of constraints be divided into the subset $\{H_n\}$, comprising all of the dynamic constraints and the remainder, say the set of operators $B_r, B_s, B_t, \ldots$. The initial state is thus described by

$$\rho(t_0) = \exp\left(-\sum_n \lambda_n(t_0) H_n - \sum_r \lambda_r(t_0) B_r\right). \tag{2.43}$$

We need to prove that the additional constraints are present if and only if they are present in $\rho(t_0)$, i.e., only if at least one of the Lagrange parameters $\lambda_r(t_0)$, $\lambda_s(t_0)$, etc., are nonzero.

By construction, the operators H_n evolve only into other operators that are elements of the dynamical algebra. Hence, $UA_iU^\dagger = \sum G_{ji} A_j$ [cf. Eq. (2.17)] now reads

$$UH_nU^\dagger = \sum_m G_{mn} H_n, \tag{2.44}$$

and all the elements of the type G_{sn} are identically zero. But for the additional operators

$$UB_rU^\dagger = \sum_m G_{mr} H_m + \sum_s G_{sr} B_s. \tag{2.45}$$

The $\underline{G}$ matrix can thus be arranged to have a block of zeros

$$\underline{G} = \begin{pmatrix} \underline{G}^{H,H} & \underline{G}^{H,B} \\ 0 & \underline{G}^{B,B} \end{pmatrix}, \tag{2.46}$$

where $\underline{G}^{H,H}$ is the matrix elements G_{mn}, $\underline{G}^{H,B}$ the matrix of elements G_{mr}, and $\underline{0}$ is the matrix of zeros corresponding to the matrix elements G_{sn}. The same block structure obtains for $\underline{G}^{-1}$,

$$\underline{G}^{-1} = \begin{pmatrix} (\underline{G}^{H,H})^{-1} & (\underline{G}^{-1})^{H,B} \\ 0 & (\underline{G}^{B,B})^{-1} \end{pmatrix}, \tag{2.47}$$

with $(\underline{G}^{-1})^{H,B} = -(\underline{G}^{H,H})^{-1}\underline{G}^{H,B}(\underline{G}^{B,B})^{-1}$.

The time evolution of the expectation values [cf. Eq. (2.27)] implied by the form of $\underline{G}^{-1}$

$$\langle \underline{H} \rangle(t) = \langle \underline{H} \rangle(t_0)(\underline{G}^{H,H})^{-1}, \tag{2.48}$$

$$\langle \underline{B} \rangle(t) = \langle \underline{B} \rangle(t_0)(\underline{G}^{B,B})^{-1} + \langle \underline{H} \rangle(t_0)(\underline{G}^{-1})^{H,B}, \tag{2.49}$$

verifies what is already evident from the operator equations, Eqs. (2.44) and (2.45). The expectation values of the dynamic constraints at any time t depend only on their initial values and on the dynamical block of the $\underline{G}$ matrix, (i.e., $\underline{G}^{H,H}$. It will be shown that $\underline{G}^{H,H}$ is dependent only on the dynamic constraints). The other constraints have no influence whatever on the evolution of the dynamic constraints. The additional constraints contribute at time t if and only if one (or more) of them were required to specify the initial state.

As before, the Lagrange parameters transform in an opposite manner to that of the constraints [compare Eq. (2.27) to Eq. (2.18)]. Thus, if we arrange the Lagrange parameters as two column vectors then, with the form, Eq. (2.46), for $\underline{G}$

$$\underline{\lambda}_H(t) = \underline{G}^{H,H}\underline{\lambda}_H(t_0) + \underline{G}^{H,B}\underline{\lambda}_B(t_0), \tag{2.50}$$

$$\underline{\lambda}_B(t) = \underline{G}^{B,B}\underline{\lambda}_B(t_0). \tag{2.51}$$

The result, Eq. (2.50), brings out one point which is possibly not evident from Eq. (2.48). Even if initially no dynamic constraints are required [so that $\underline{\lambda}_H(t_0) = 0$] they may contribute during the collision, $[\underline{\lambda}_H(t) \neq 0]$. Not so for the additional constraints. If they were not initially required [i.e., if $\underline{\lambda}_B(t_0) = 0$] they will continue to be absent at all subsequent times.

III. EXAMPLES

As illustrations of the method we solve two simple collision problems, obtaining explicit results for the final-state distribution and for the $\underline{S}$-matrix elements. Our aim is not only to apply the techniques of Sec. II, but also to introduce the more abstract ideas of Secs. IV and V in a concrete context before discussing them in more general terms. We shall thus refer ahead and would like to invite the reader to return to this section after he has examined the rest of the paper.

A. Forced harmonic oscillator

Consider a harmonic oscillator (a molecule or a vibrational nucleus) acted upon by an external time-dependent force. This force can be taken as due to the perturbation induced by a structureless

particle moving along a classical trajectory. The model has been used in both molecular[21] and nuclear[13] physics and the scattering matrix for the problem is available in closed form.[20] The same Hamiltonian has also been extensively discussed in quantum optics,[19] leading to such results as[22] "an initial coherent state will always remain coherent."

Introducing reduced position (Q) and momentum (P) operators $P=(m\hbar\omega)^{-1/2}p$, $Q=(m\omega/\hbar)^{1/2}q$, we can write the Hamiltonian $H=H_0+V$ as

$$H_0=\hbar\omega(P^2/2+Q^2/2),$$
$$V=F(t)q=2^{1/2}\hbar f(t)Q. \tag{3.1}$$

Here ω and m are the frequency and mass of the oscillator and $f(t)$ defined via Eq. (3.1) has the dimensions of frequency. An alternative expression for H in terms of creation and annihilation operators $a=2^{-1/2}(Q+iP)$, $a^\dagger=2^{-1/2}(Q-iP)$ is

$$H(t)=\hbar\omega a^\dagger a+\hbar[f(t)a+f^*(t)a^\dagger], \tag{3.2}$$

where we have shifted the zero of energy by $\frac{1}{2}\hbar\omega$ and have allowed for a more general coupling term,[19, 22] [in Eq. (3.1) $f(t)$ is real].

The dynamical algebra generated by the Hamiltonian is obtained by examining the commutation relations between all the operators that appear in $H(t)$. Putting $N=a^\dagger a$,

$$[N,a]=-a,[N,a^\dagger]=a^\dagger,[a,a^\dagger]=I. \tag{3.3}$$

The only new operator that appears is the identity I which commutes with all the others. The dynamical algebra is thus four dimensional and consists of four operators I, $a^\dagger$, a, N.

The matrix $\underline{\alpha}$ [cf. Eq. (2.13)] is now immediately available. Using the commutation relations [Eq. (3.3)] and the order I, $a^\dagger$, a, N

$$\underline{\alpha}=\hbar\begin{bmatrix}0 & f(t) & -f^*(t) & 0\\ 0 & \omega & 0 & -f^*(t)\\ 0 & 0 & -\omega & f(t)\\ 0 & 0 & 0 & 0\end{bmatrix}. \tag{3.4}$$

Say now the initial state is a thermal distribution over the oscillator states. Then

$$\rho(t_0)=e^{[-\beta(t_0)N-\lambda_0(t_0)]}. \tag{3.5}$$

Here $\beta(t_0)=\hbar\omega/kT$, where T is the initial temperature and λ_0, the Lagrange parameter conjugate to the identity operator, is, as always,[37, 38] the logarithm of the partition function. The set of constraints is constructed by starting with N and I (which are present at t_0) and, by taking their commutators with H (and so on, see another example in Sec. III C below), obtaining a set of operators that is closed under commutation with H. Since N is an element of the dynamical algebra the set of constraints coincides (for this case) with the dynamic algebra. Hence, for subsequent times t [cf. Eq. (2.11)],

$$\rho(t)=\exp[-\beta(t)N-\gamma(t)a^\dagger-\gamma^*(t)a-\lambda_0(t)] \tag{3.6}$$

There are four $[\beta(t), \mathrm{Re}\gamma(t), \mathrm{Im}\gamma(t), \lambda_0(t)]$ time-dependent Lagrange parameters. Their equations of motion, Eqs. (2.16), are specified by the matrix $\underline{\alpha}$,

$$\frac{\partial\beta(t)}{\partial t}=0,$$
$$\frac{\partial\gamma(t)}{\partial t}=-i\omega\gamma(t)+if^*(t)\beta(t),$$
$$\frac{\partial\gamma^*(t)}{\partial t}=i\omega\gamma^*(t)-if(t)\beta(t), \tag{3.7}$$
$$\frac{\partial\lambda_0(t)}{\partial t}=i[f^*(t)\gamma^*(t)-f(t)\gamma(t)].$$

These equations can be readily integrated (for reasons which will be discussed below). In particular we note that the Lagrange parameter of (the reduced energy) N is time independent and the complete solution of Eq. (3.7) is

$$\beta(t)=\beta(t_0),$$
$$\gamma(t)=e^{(-i\omega\Delta t)}[\gamma(t_0)-\alpha(t,t_0)\beta(t_0)],$$
$$\gamma^*(t)=e^{(i\omega\Delta t)}[\gamma^*(t_0)-\alpha^*(t,t_0)\beta(t_0)],$$
$$\lambda_0(t)=\lambda_0(t_0)-\alpha^*(t,t_0)\gamma(t_0)-\alpha(t,t_0)\gamma^*(t_0)+|\alpha(t,t_0)|^2\beta(t_0). \tag{3.8}$$

Here $\gamma(t_0)=\gamma^*(t_0)=0$ for the initial state, Eq. (3.5), $\Delta t=t-t_0$ and

$$\alpha(t,t_0)=-i\int_{t_0}^{t}f^*(\tau)e^{i\omega\tau}d\tau. \tag{3.9}$$

The solution, Eq. (3.8), has an obvious formal disadvantage. The Lagrange parameters become rapidly oscillating functions of time as Δt increases. Yet these oscillations are "uninteresting" being the reflection of time evolution under the unperturbed Hamiltonian. By going over to the interaction picture these oscillations will be factored out [cf. Eq. (3.36) below].

There is a corresponding set of equations of motion [cf. Eq. (2.19)] and their solution for the mean values of the constraints [i.e., $\langle I\rangle(t)\equiv 1$, $\langle a^\dagger\rangle(t)$, $\langle a\rangle(t)$, and $\langle N\rangle(t)$].

In conclusion, an initial state of the form[39]

$$\rho = \exp[-\beta N - \gamma a^\dagger - \gamma^* a - \lambda_0]$$
$$\equiv \exp[-\beta(a^\dagger - w^*)(a - w) - \lambda_0]$$
$$\equiv \exp[-\beta N - \lambda_p P - \lambda_Q Q - \lambda_0]$$
$$\equiv \exp\{-\tfrac{1}{2}\beta[(P-\mu_p)^2 + (Q-\mu_Q)^2] - \tilde{\lambda}_0\} \qquad (3.10)$$

[with $-\gamma = \beta w$, $\lambda_p = -\beta\mu_p = i(\gamma^* - \gamma)/2^{1/2}$, $\lambda_Q = -\beta\mu_Q = (\gamma^* + \gamma)/2^{1/2}$, $\tilde{\lambda}_0 = \lambda_0 - \frac{1}{2}\beta(\mu_p^2 + \mu_Q^2 + 1)$] will always retain this functional form since the set of constraints is identical to the dynamical algebra. The time evolution will only change the values of the Lagrange parameters, except that β [cf. Eq. (3.8)] will not vary with time, and that $w(t) = w(t_0) + \alpha(t, t_0)$.

B. Information theory

For the problem of the forced harmonic oscillator the results obtained are as follows: Say the initial state is thermal, Eq. (3.5). Then, the initial partition function is well known, $e^{(\lambda_0)} = (1 - e^{(-\beta)})^{-1}$, where $\beta = \hbar\omega/kT$ or

$$\lambda_0 = -\ln(1 - e^{(-\beta)}) . \qquad (3.11)$$

At later times Eq. (3.8) gives, with $\lambda_0(t) = \lambda_0'$

$$\lambda_0' = \lambda_0 + |\alpha|^2\beta = \lambda_0 + |w|^2\beta = \lambda_0 + |\gamma|^2/\beta . \qquad (3.12)$$

We now have $\lambda_0(t)$ as a function of the three other Lagrange parameters β [which is not changing with time, cf. Eq. (3.8)], γ, and γ^*.

For the mean values of the constraints we have

$$\langle N\rangle = \frac{-\partial\lambda_0'}{\partial\beta} = |\gamma|^2\beta^{-2} + (e^{(-\beta)} - 1)^{-1} ,$$
$$\langle a^\dagger\rangle = 2^{-1/2}(\langle Q\rangle - i\langle P\rangle) = \frac{\partial\lambda_0'}{\partial\gamma} = \frac{-\gamma^*}{\beta} , \qquad (3.13)$$
$$\langle a\rangle = 2^{-1/2}(\langle Q\rangle + i\langle P\rangle) = \frac{-\partial\lambda_0'}{\partial\gamma^*} = \frac{-\gamma}{\beta} ,$$
$$\tfrac{1}{2}(\langle P\rangle^2 + \langle Q\rangle^2) = |\gamma|^2/\beta^2 = |\alpha|^2 .$$

These equations can be inverted (if so desired) to yield the Lagrange parameters in terms of the constraints

$$\beta = \ln\{1 + [\langle N\rangle - (\langle P\rangle^2 + \langle Q\rangle^2)]^{-1}\} ,$$
$$\beta^{-1}\mathrm{Re}(\gamma) = \langle Q\rangle \cdot 2^{-1/2} \text{ or } \beta^{-1}\lambda_Q = -\langle Q\rangle , \qquad (3.14)$$
$$\beta^{-1}\mathrm{Im}(\gamma) = -\langle P\rangle 2^{-1/2} \text{ or } \beta^{-1}\lambda_p = -\langle P\rangle .$$

The reason we do not have to worry about whether the partition function exists[30] is that the partition function exists when $\rho(t)$ can be normalized. But $\mathrm{Tr}\{\rho(t)\}$ is invariant in time, $\mathrm{Tr}\{\rho(t)\} = \mathrm{Tr}\{U\rho(t_0)U^\dagger\} = \mathrm{Tr}\{U^\dagger U\rho(t_0)\} = \mathrm{Tr}\{\rho(t_0)\}$. Hence, if we specified an acceptable initial state, the rest is assured. Just to be on the safe side, we verify that if $\rho(t_0)$ can be normalized then β should be positive or [cf. Eq. (3.14)] that $\langle N\rangle > \frac{1}{2}(\langle P\rangle^2 + \langle Q\rangle^2)$. But since $N = \frac{1}{2}(\langle P^2\rangle + \langle Q^2\rangle) + \frac{1}{2}i\langle[Q,P]\rangle$, the normalization condition is indeed inherently satisfied, being an immediate implication of the Heisenberg uncertainty principle.[6] To see this explicitly, note that if we define $(\Delta P)^2 = \langle P^2\rangle - \langle P\rangle^2 \geq 0$ and similarly for $(\Delta Q)^2$ then the uncertainty principle is[22]

$$2(\Delta P)(\Delta Q) \geq |\langle[Q,P]\rangle| . \qquad (3.15)$$

Now, since $(a-b)^2 \geq 0$,

$$(\Delta P)^2 + (\Delta Q)^2 \geq 2(\Delta P)(\Delta Q) \geq |\langle[Q,P]\rangle| , \qquad (3.16)$$

and the end inequalities in Eq. (3.16) are the normalization condition.

C. Nondynamic constraints

We have thus far considered initial states of a special type, where the constraints required to specify the state are all dynamic constraints, i.e., are all elements of the dynamical algebra. Say now N^2 is required to specify the initial state. This will be the case if one wants an initial state where the oscillator eigenstates are clustered about some mean value, for example,

$$\rho(t_0) = \exp[-\eta(t_0)(N - n_0)^2 - \lambda_0(t_0)] . \qquad (3.17)$$

If we let $\eta(t_0) \to \infty$, only the state with $n = n_0$ will contribute to $\rho(t_0)$.

The set of constraints for $\rho(t_0)$ need now be obtained. We first take the commutator of N^2 with all elements of the dynamical algebra $(I, a, a^\dagger, N)$. Only a and $a^\dagger$ give rise to nonvanishing commutators

$$[a^\dagger, N^2] = -a^\dagger - 2a^\dagger N ,$$
$$[a, N^2] = a + 2Na. \qquad (3.18)$$

The operators $a^\dagger$, $a^\dagger N$, a, and Na are thus possible constraints (i.e., they can evolve out of N^2). The operators that can evolve out of $a^\dagger N$ and Na are determined by taking their commutators with the elements of the dynamical algebra,

$$[N, a^\dagger N] = a^\dagger N, \quad [N, Na] = -Na ,$$
$$[a, a^\dagger N] = 2N, \quad [a, Na] = a^2, \qquad (3.19)$$
$$[a^\dagger, a^\dagger N] = -a^{\dagger 2}, \quad [a^\dagger, Na] = -2N .$$

Three new operators a^2, $a^{\dagger 2}$, and $N = a^\dagger a$ are obtained in Eq. (3.19) as additional constraints. Taking their commutator with the elements of the dynamical algebra, we obtain no new operators. Starting with N^2 and the identity as the only constraints in the initial state, we have generated a closed set of nine constraints: $I, a, a^\dagger, N, a^2, a^{\dagger 2}, a^\dagger N, Na, N^2$.

We shall shortly determine the G matrix [cf. Eq. (3.38) below] and hence $\rho(t)$ for this problem. Be-

fore that we need raise a more general question. Does the number of independent parameters in the solution indeed increase or does the number of parameters reflect the number of dynamic constraints, and hence is the same for all possible initial states of the family of similar collisions. The latter is, as expected, the correct conclusion.

D. Time evolution in the interaction picture

The new concepts of the $\underline{G}$ matrix in the interaction picture and the G matrix as a function of the "group parameters" are introduced in this section as means of further simplifying the solution of the forced harmonic-oscillator problem. A general discussion is provided in Sec. IV.

The key formal tool will be the following expansion[17, 36] for two linear operators A and B

$$e^{(A)}Be^{(-A)} = B + [A,B] + (1/2!)[A,[A,B]] + (1/3!)[A,[A,[A,B]]] + \cdots = \sum_{j=0} (j!)^{-1}(adA)^j B = e^{(adA)}B, \quad (3.20)$$

which is derived from the Baker-Hausdorff expansion.[17, 36] The notation (adA) denotes a (linear) operator such that[40]

$$(adA)B = [A,B], \quad (adA)^2 B = [A,[A,B]] \quad (3.21)$$

etc.

Taking the interaction picture to coincide with the Schrödinger picture at the time $t=0$, the potential in the interaction picture (when H_0 is time independent) is given by

$$V_I(t) = e^{(iH_0t/\hbar)}V(t)e^{-iH_0t/\hbar} = e^{[(it/\hbar)(adH_0)]}V(t). \quad (3.22)$$

The operators a and $a^\dagger$ are eigenoperators of adH_0.

$$(adH_0)a \equiv [H_0, a] = -\hbar\omega a,$$
$$(adH_0)a^\dagger \equiv [H_0, a^\dagger] = \hbar\omega a^\dagger. \quad (3.23)$$

Therefore they are also eigenoperators of $\exp[(it/\hbar)(adH_0)]$.

$$e^{[(it/\hbar)(adH_0)]}a = e^{(-i\omega t)}a,$$
$$e^{[(it/\hbar)(adH_0)]}a^\dagger = e^{(i\omega t)}a^\dagger. \quad (3.24)$$

The determination of the potential in the interaction picture using $V(t)$ from Eqs. (3.2) and (3.24) is thus immediate:

$$V_I(t) = \hbar[f(t)ae^{(-i\omega t)} + f^*(t)a^\dagger e^{(i\omega t)}]. \quad (3.25)$$

The elements of the dynamical algebra in the interaction picture are the elements of the algebra generated by a and $a^\dagger$. Since $[a,a^\dagger] = I$, the algebra consists of three operators: $I, a, a^\dagger$. It is three dimensional.

In terms of the elements of the dynamical algebra the evolution operator can be written as [cf. Eq. (4.3) below]

$$U_I(t) = \exp[\alpha(t)a^\dagger - \alpha^*(t)a + i\mu(t)I], \quad (3.26)$$

where $\alpha(t)$ is a complex parameter and $\mu(t)$ is real. The three real parameters in $U_I(t)$ are referred to as the parameters of the (dynamical) group. We shall obtain explicit results for their time dependence (cf. Sec. III F) but first, we evaluate the $\underline{G}$ matrix in the interaction picture.

E. $\underline{G}$ matrix

For any set of constraints the $\underline{G}$ matrix is defined by

$$UA_rU^\dagger = \sum_s A_s G_{sr}. \quad (3.27)$$

The motivation for the introduction of the "group parameters" is now clear. Irrespective of the number of constraints in the set, the $\underline{G}$ matrix is a function only of the group parameters whose number equals the dimension of the dynamic algebra. Even when additional (i.e., nondynamic) constraints need be introduced, the evolution operator and hence $\underline{G}$ depend only on the parameters of the group (and these are the parameters of the dynamic constraints[41] alone).

Using the expansion, Eq. (3.20), to evaluate Eq. (3.27) one finds that for the dynamic constraints the expansion terminates after the first commutator

$$Ua^\dagger U^\dagger = \exp[\alpha(ada^\dagger) - \alpha^*(ada) + i\mu(adI)]a^\dagger = a^\dagger + [\alpha a^\dagger - \alpha^* a + i\mu, a^\dagger] = a^\dagger - \alpha^*$$
$$UaU^\dagger = a - \alpha, \quad UIU^\dagger = I. \quad (3.28)$$

Hence the $\underline{G}$ matrix in the interaction picture is

$$\underline{G}^I = \begin{bmatrix} 1 & -\alpha^* & -\alpha \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (3.29)$$

$\underline{G}^I$ has the upper triangular form expected (cf. Sec. V G) for a solvable dynamical algebra.

The set $\{I, a, a^\dagger\}$ is also invariant under commutation with H_0. In Sec. IV C the $\underline{G}$ matrix in the Schrödinger picture will be expressed in the form $\underline{G}^0\underline{G}^I$. The $\underline{G}^0$ matrix is defined by

$$e^{(-iH_0t/\hbar)}A_r e^{(iH_0t/\hbar)} = \sum_s G^0_{sr}A_s, \quad (3.30)$$

[and is hence the $\underline{G}$ matrix for the Hamiltonian H_0; compare Eq. (3.31) to Eq. (2.30)] and $\underline{G}^I$, the $\underline{G}$

matrix in the interaction picture, is all that is required to determine ρ_{out}, the density operator for $t\to\infty$. Using Eq. (3.24) we can write G^0 immediately for any time interval Δt

$$\underline{G}^0=\begin{bmatrix}1 & 0 & 0\\ 0 & e^{(-i\omega\Delta t)} & 0\\ 0 & 0 & e^{(i\omega\Delta t)}\end{bmatrix}. \tag{3.31}$$

When we multiply $\underline{G}^0$ by $\underline{G}^I$, the resulting $\underline{G}$ matrix has strongly oscillatory diagonal elements and no definite limit as $\Delta t\to\infty$, in contrast to $\underline{G}^I$ which is well defined in that limit.

Appendix A provides a general proof that the $\underline{G}^0$ matrix will have oscillatory matrix elements whenever H_0 is time independent.

To solve for the evolution of an initially thermal state we start with N and I as the only initial constraints. In the interaction picture N is not an element of the dynamical algebra but $[V_I,N]$ is in the algebra so that the set of constraints is $I, a, a^\dagger, N$. To compute $\underline{G}^I$ we only need to compute $U_I N U_I^\dagger$. Putting $U_I=e^{(A)}$ and using Eq. (3.26) for U_I

$$\begin{aligned}&[A,N]=[\alpha a^\dagger-\alpha^* a,N]=-\alpha a^\dagger-\alpha^* a,\\ &[A,[A,N]]=[\alpha a^\dagger-\alpha^* a,-\alpha a^\dagger-\alpha^* a]=2|\alpha|^2,\\ &[A,[A,[A,N]]]=0.\end{aligned} \tag{3.32}$$

Thus

$$U_I N U_I^\dagger=N-\alpha a^\dagger-\alpha^* a+|\alpha|^2. \tag{3.33}$$

Ordering the constraints as $I, a^\dagger, a, N$ and using Eqs. (3.29) and (3.33)

$$\underline{G}^I=\begin{bmatrix}1 & -\alpha^* & -\alpha & |\alpha|^2\\ 0 & 1 & 0 & -\alpha\\ 0 & 0 & 1 & -\alpha^*\\ 0 & 0 & 0 & 1\end{bmatrix}. \tag{3.34}$$

Since N is not a dynamic constraint (in the interaction picture), $\underline{G}^I$ has the structure noted in Eq. (2.46). In particular, since $G_{N,N}=1$, the Lagrange parameter of N is time independent. The set of constraints is also invariant under H_0. H_0 and N commute and using Eq. (3.32)

$$\underline{G}^0=\begin{bmatrix}1 & & & \\ & e^{(-i\omega\Delta t)} & 0 & \\ & 0 & e^{(i\omega\Delta t)} & \\ & & & 1\end{bmatrix}. \tag{3.35}$$

One can now obtain the matrix $\underline{G}$

$$\underline{G}=\begin{bmatrix}1 & -\alpha^* & -\alpha & |\alpha|^2\\ 0 & e^{(-i\omega\Delta t)} & 0 & -\alpha e^{(-i\omega\Delta t)}\\ 0 & 0 & e^{(i\omega\Delta t)} & -\alpha^* e^{(i\omega\Delta t)}\\ 0 & 0 & 0 & 1\end{bmatrix}, \tag{3.36}$$

and verify, using the general result $\underline{\lambda}(t)=\underline{G}(t,t_0)\underline{\lambda}(t_0)$, $\Delta t=t-t_0$ that Eq. (3.36) is indeed equivalent to the result Eq. (3.8), of direct integration. The novel point is that all the oscillatory time dependence of $\underline{G}$ has been factored out by working in the interaction picture, and as discussed in Sec. IV C, $\underline{G}^I$ suffices to determine the distribution of final states.

When N^2 say is an initial constraint we need to compute $UA_\gamma U^\dagger$ for $A_\gamma=a^{\dagger 2}$, a^2, $a^\dagger N$, Na, and N^2. Putting $U^I=e^{(A)}$, using the expansion (3.20) and using Eq. (3.26) for U^I, the procedure is quite straightforward. For example,

$$\begin{aligned}&[A,a^{\dagger 2}]=[\alpha a^\dagger-\alpha^* a,a^{\dagger 2}]=-2\alpha^* a^\dagger,\\ &[A,[A,a^{\dagger 2}]]=[\alpha a^\dagger-\alpha^* a,-2\alpha^* a^\dagger]=2\alpha^{*2},\\ &[A,[A,[A,a]]]=0,\end{aligned} \tag{3.37}$$

or

$$U_I a^{\dagger 2} U_I^\dagger=a^{\dagger 2}-2\alpha^* a^\dagger+\alpha^{*2}. \tag{3.38}$$

Proceeding in this fashion we obtain the $\underline{G}^I$ matrix.

F. Equation of motion for the group parameters

The only parameters in the $\underline{G}$ matrices are the group parameters in U. Moreover, as expected, the phase factor [denoted by μ in Eq. (3.26)] in the evolution operator does not appear in $\underline{G}$. The equations of motion for the group parameters are considered in Sec. V E. For the present problem Eq. (5.16) is of the form

$$\int_0^1 dx\begin{bmatrix}1 & -x\alpha^* & -x\alpha\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-d\mu/dt\\ i\,d\alpha/dt\\ -i\,d\alpha^*/dt\end{bmatrix}=\begin{bmatrix}0\\ f^*(t)\,e^{(i\omega t)}\\ f(t)\,e^{(-i\omega t)}\end{bmatrix}.$$

Performing the integration over x

$$\begin{bmatrix}1 & -\frac{1}{2}\alpha^* & -\frac{1}{2}\alpha\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-\dot\mu\\ i\dot\alpha\\ -i\dot\alpha^*\end{bmatrix}=\begin{bmatrix}0\\ f^*(t)e^{(i\omega t)}\\ f(t)e^{(-i\omega t)}\end{bmatrix}.$$

or $i\dot\alpha=f^*(t)e^{(i\omega t)}$ with the boundary condtion $\alpha(t_0,$

$t_0) = 1$. We recover our previous result, Eq. (3.9). What have we gained? To begin with, it is not necessary to know $\alpha(t, t_0)$ as a function of t in order to determine the $\underline{G}$ matrix and hence $\underline{\lambda}[\alpha(t, t_0)]$. Moreover, we have explicit illustrations that for three different sets of constraints the $\underline{G}$ matrices [Eqs. (3.29), (3.36), and (3.38)] depend only on the parameters of the group.

G. Scattering matrix and the density matrix

The technique of group representation (discussed in general in Sec. V) is employed to obtain explicit results for the scattering matrix and the final density matrix (for a thermal initial state) of the forced harmonic oscillator. The derivation is done in detail which will not be repeated for the case of rotational excitation (Sec. III K and Appendix B).

Miller[42] introduces a Lie group S_4 (Sec. 4.11 of Ref. 42) and its (λ, l) unitary representation (Sec. 4.14 of Ref. 42). There are four elements in the Lie algebra and their (λ, l) representation ($l > 0$, λ integer) is (in Miller's notation)

$$\begin{aligned} J^3\psi_n &= (n-\lambda)\psi_n, \\ E\psi_n &= l\psi_n, \\ J^+\psi_n &= [l(n+1)]^{1/2}\psi_{n+1}, \\ J^-\psi_n &= [ln]^{1/2}\psi_{n-1}. \end{aligned} \tag{3.39}$$

For $\lambda = 0, l = 1$ we can make the identification $J^3 \leftrightarrow N = a^\dagger a$, $E \leftrightarrow I$, $J^+ \leftrightarrow a^\dagger$, $J^- \leftrightarrow a$. It follows that we can use the (0, 1) unitary representation of S_4 to obtain the matrix elements of the evolution operator. Miller works with the product representation (p. 116 of Ref. 42) of the group elements (Sec. IV A). Using the standard result

$$e^{(A+B)} = e^{(A)}e^{(B)}e^{(-[A,B]/2)},$$

where $[A, [A,B]] = [B, [A,B]] = 0$ we obtain

$$U_I = e^{(\alpha a^\dagger - \alpha^* a + i\mu)} = e^{(\alpha a^\dagger)}e^{(-\alpha^* a)}e^{(i\mu - |\alpha|^2/2)}, \tag{3.40}$$

or, in Miller's notation

$$= e^{(ixP/2^{1/2})}e^{(-iyQ/2^{1/2})}e^{[i(\mu + xy/4)]},$$

where α corresponds to $-\frac{1}{2}(x - iy)$ or equivalently to $-re^{(i\theta)}$ in the notation of Ref. 42, Eq. (4.123). Thus

$$\langle n|U_I|m\rangle = e^{(i\mu)}e^{(-|\alpha|^2/2)}(n!/m!)^{1/2} \times (-\alpha^*)^{m-n}L_n^{m-n}(|\alpha|^2). \tag{3.41}$$

Here $L_s^k(Z)$, with k, s integers, $k + s \geq 0$ are the associated Laguerre polynomials. Taking the magnitude of $\alpha(t, t_0)$ for $t \to \infty$, $t_0 \to -\infty$ [(cf. Eq. (3.9)], Eq. (3.41) yields the well-known[20] result for the $\underline{S}$ matrix of the forced harmonic-oscillator problem.

To derive a less standard result consider a thermal initial state $\rho_{in} = e^{(-\beta N - \lambda_0)}$, $e^{(-\lambda_0)} = 1 - e^{(-\beta)}$, then we saw that [cf. Eq. (3.10)] the final state after the collision is

$$\rho_{out} = \exp\{-\beta[N - \alpha a^\dagger - \alpha^* a + |\alpha|^2] - \lambda_0\}. \tag{3.42}$$

Using the product-form representation

$$\rho_{out} = e^{(-\beta N)}e^{(\gamma_+ a^\dagger)}e^{(\gamma_- a)}e^{(\delta)}, \tag{3.43}$$

one finally obtains[43]

$$\begin{aligned} \gamma_+ &= 2\alpha e^{(\beta/2)}\sinh(\tfrac{1}{2}\beta), \\ \gamma_- &= 2\alpha^* e^{(-\beta/2)}\sinh(\tfrac{1}{2}\beta), \\ \delta &= -|\alpha|^2(1 - e^{(-\beta)}) - \lambda_0. \end{aligned} \tag{3.44}$$

The product form Eq. (3.43) enables us to recognize ρ_{out} as an element of the complex Lie group denoted as $G(0, 1)$ by Miller.[42] (This is just a complex version of the real Lie group S_4). Using Eq. (4.26) of Ref. 42,

$$\langle n|\rho_{out}|m\rangle = (n!/m!)^{1/2}e^{(\delta)}e^{(-\beta n)}(\gamma_-)^{m-n}L_n^{m-n}(-\gamma_+\gamma_-). \tag{3.45}$$

As a check of this result consider the $\beta \to \infty$ limit, corresponding to the oscillator being initially in the ground state. Now [cf. Eq. (3.44)]

$$\gamma_+\gamma_- = (1 - e^{(-\beta)})^2 e^{(\beta)}|\alpha|^2, \tag{3.46}$$

and using the explicit polynomial expression for the Laguerre $L_n = L_n^0$

$$\lim_{\beta\to\infty} e^{(-\beta n)}L_n(-\gamma_+\gamma_-) \to |\alpha|^{2n}/n!, \tag{3.47}$$

or

$$\langle n|\rho_{out}|n\rangle \xrightarrow[\beta\to\infty]{} e^{(-|\alpha|^2)}|\alpha|^{2n}/n!. \tag{3.48}$$

Equation (3.48) is the known result for an oscillator that is initially in the ground state.

H. Classical probability and the classical limit of the quantal probability

Starting with a thermal initial state, the classical density function at later times is [cf. Eq. (3.10)]

$$\rho(P, Q) = \exp(-\beta N - \lambda_Q Q - \lambda_p P - \lambda_0), \tag{3.49}$$

where N is the classical reduced-oscillator Hamiltonian, $N + \frac{1}{2} = \frac{1}{2}(P^2 + Q^2)$. To compare Eq. (3.49) with the quantal result, Eq. (3.45), for $\langle n|\rho|n\rangle$ it is necessary to integrate Eq. (3.49) over a region in phase space defined by

$$n \leq \tfrac{1}{2}(P^2 + Q^2) \leq n + 1. \tag{3.50}$$

More precise correspondence rules can, of course, be provided[45] but the simple prescription, Eq. (3.50), will suffice for our purpose. To carry

the required integration it is convenient to introduce action J and angle θ variables in the usual manner $P=(2J)^{1/2}\sin(\theta)$, $Q=(2J)^{1/2}\cos(\theta)$ so that $dPdQ=dJd\theta$ and $N=J-\frac{1}{2}$. We further define r and ϕ by $r\cos\phi=(2J)^{1/2}\lambda_Q$, $r\sin\phi=(2J)^{1/2}\lambda_p$, and using Eqs. (3.13) and (3.14), $r=[2J(\lambda_Q^2+\lambda_p^2)]^{1/2}=2J^{1/2}\beta|\alpha|$. With these changes

$$\rho(J,\theta)=\exp[-\beta N-r\cos(\theta-\phi)-\lambda_0]\,. \tag{3.51}$$

To integrate over the region specified by Eq. (3.50) we need to integrate over θ from 0 to 2π and over J from n to $n+1$. The first part is immediate,

$$\int_0^{2\pi} d\theta\exp[-\beta N-r\cos(\theta-\phi)-\lambda_0] = e^{[-\beta N-\lambda_0]}(2\pi)J_0(ir)\,, \tag{3.52}$$

where J_0 is the Bessel function of zeroth order. The integration over J is hard (since r is a function of J) and so will be done by the mean value theorem. The integral of Eq. (3.52) over J from n to $n+1$ is simply the integrand evaluated at $J\simeq n+\frac{1}{2}$ (i.e., $N=n$). Finally, we need the partition function. At $t\to-\infty$ this is just the classical thermal result $e^{(\lambda_0)}=2\pi/\beta$. At later times [cf. Eq. (3.12)] this is

$$e^{(\lambda_0)}=(2\pi/\beta)\,e^{(|\gamma|^2/\beta)}\,. \tag{3.53}$$

Collecting all our results, the classical probability to find the oscillator with energy in the range $(n-\frac{1}{2}+\frac{1}{2})\hbar\omega=n\hbar\omega$ to $(n+1)\hbar\omega$ is

$$P_c(n)=\beta e^{(-\beta n-\beta|\gamma|^2)}J_0(i2\beta|\alpha|\sqrt{n})\,. \tag{3.54}$$

The significance of Ref. 34 should now be obvious. Some finite effort is required to "quantize" the classical results, i.e., to bring them to a form where they can be compared with the (necessarily quantized) experimental results.

The quantal result corresponding to Eq. (3.54) is given in Eq. (3.45), $P_Q=\langle n|\rho|n\rangle$. Using the definitions, Eqs. (3.8) and (3.12),

$$P_Q(n)=(1-e^{(-\beta)})\exp[-|\alpha|^2(1-e^{(-\beta)})] \times e^{(-\beta n)}L_n[-4|\alpha|^2\sinh^2(\tfrac{1}{2}\beta)]\,. \tag{3.55}$$

To take the classical limit, we first have to go to high (reduced) temperatures, $\beta=(\hbar\omega/kT)\ll 1$, whence Eq. (3.55) reduces to

$$P_Q(n)\underset{\beta\to 0}{\longrightarrow}\beta e^{(-\beta n-\beta|\alpha|^2)}L_n(-|\alpha|^2\beta^2)\,. \tag{3.56}$$

Next, going to the limit of high quantum numbers,

$$L_n(-y^2/n)\underset{n\to\infty}{\longrightarrow}J_0(2iy)\,, \tag{3.57}$$

we see that Eq. (3.56) reduces to Eq. (3.54) with the substitution $y=|\alpha|\beta n^{1/2}$ in Eq. (3.56).

The classical limit is thus a high-temperature, high-final-quantum-numbers limit. Just going to high temperatures [i.e., Eq. (3.56)] will suffice only under the extreme condition $y^2\ll n^2$ or, explicitly, $\beta^2\ll n|\alpha|^{-2}$ which means [cf. Eq. (3.13)], where $|\alpha|^2\beta^2=|\gamma|^2/\beta^2$) that $\Delta\langle N\rangle\ll n\beta^{-2}$ in the collision.

I. Multipole rotational excitation

The (long-range) interaction between a structureless particle moving along a classical trajectory and a rotor (or a symmetric top) can be described by a time-dependent potential

$$V(t)=\sum_{l=1}\sum_{m=-l}^{l}S_{lm}^*(t)\,Q_{lm}\,. \tag{3.58}$$

Here Q_{lm} is the spherical component of the electric 2^l pole of the rotor or the top. The central ($l=0$) term in the potential governs the relative motion. Such potentials have been extensively employed in both nuclear[13,46] and molecular[47,48] collision theory. Very many of these applications also invoke the sudden approximation[24] where the collision time is assumed to be short compared to the rotation time of the top. In this approximation, Eq. (3.58) is also the potential in the interaction picture. We now consider some particular multipole so that

$$V_l(t)=\sum_{m=-l}^{l}S_{lm}^*(t)\,Q_{lm}\,. \tag{3.59}$$

The elements of the dynamical algebra are thus the set of $2l+1$ (commuting) operators Q_{lm}. The $\underline{\alpha}$ matrix for such a dynamical algebra is [cf. Eq. (2.38)] identically zero and with

$$U_I=\exp\left[-(i/\hbar)\sum_m\mu_m^*Q_{lm}\right]\,, \tag{3.60}$$

$$U_IQ_{lm}U_I^\dagger=Q_{lm}\,. \tag{3.61}$$

The G^I matrix representation of the dynamical algebra is simply the unit matrix. It follows that

$$\mu_m^*(t)=\int_{-\infty}^{t}S_{lm}(t')dt'\,. \tag{3.62}$$

We shall treat the general case elsewhere and now continue to examine the $l=1$ (dipole) case. It is then possible to regard the three group parameters (the μ's) as components of a vector $\underline{\mu}$. When the colliding particle follows a classical trajectory determined by a central potential the motion is confined to a plane. The component of $\underline{\mu}$ perpendicular to this plane will vanish. To see this, note that for a central potential (say of the form r^{-n}, where r is the relative separation)

$$\underline{\mu}(t) \propto \int_{-\infty}^{t} [\underline{r}(t)/r^{n+1}(t)]dt\,. \tag{3.63}$$

It also follows that if n is odd (e.g., Coulomb excitation) it is possible to choose a coordinate system such that a second component of $\underline{\mu}$ will vanish at $t \to \infty$. The one component of $\underline{\mu}$ that will survive after the collision is the one along the apex line of the trajectory (i.e., μ_z in coordinate system B of Alder and Winter[13]).

J. $\underline{G}$ matrix for a dipole

Say the initial state is thermal. The Hamiltonian of a dipole is of the form $L^2/2I$, where I is the moment of inertia and L is the angular momentum in the space frame. We require an invariant set generated by L^2. If all we require is the matrix for $t \to +\infty$, the set should be closed under commutation with Q_z only (since for $t \to \infty$, $\mu_x = \mu_y = 0$ when the z axis is suitably chosen). A somewhat tedious computation yields

$$[L^2, Q_z] = 2Q_z + (Q_- L_+ - Q_+ L_-)\,. \tag{3.64}$$

Here

$$L_\pm = L_x \pm iL_y\,, \tag{3.65}$$

and similarly for Q's

$$Q_\pm = Q_x \pm iQ_y, \quad Q_0 = Q_z\,. \tag{3.66}$$

The $Q_\pm$'s and $Q_z = Q_0$ are the spherical components of the dipole vector operator.[49] The new operators in the first round, Eq. (3.64), are $Q_+ L_-$ and $Q_- L_+$, and in the second round

$$[Q_- L_+, Q_z] = Q_-[L_+, Q_z] = -Q_- Q_+ = -Q_+ Q_-\,. \tag{3.67}$$

The new operator is $Q_+ Q_-$. In the third round

$$[Q_- Q_+, Q_z] = 0\,, \tag{3.68}$$

and the set $L^2, Q_z, Q_+ L_-, Q_- L_+, Q_+ Q_-$ (and I) is closed under commutation with Q_z. The $\underline{G}_I(t \to \infty)$ matrix is 6×6

$$\begin{array}{c} \\ I \\ Q_z \\ Q_+Q_- \\ Q_-L_+ \\ Q_+L_- \\ L^2 \end{array} \begin{array}{c} \begin{array}{cccccc} I & Q_z & Q_+Q_- & Q_-L_+ & Q_+L_- & L^2 \end{array} \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ & 1 & 0 & 0 & 0 & 2ir \\ & & 1 & -ir & ir & r^2 \\ & \underline{0} & & 1 & 0 & ir \\ & & & & 1 & -ir \\ & & & & & 1 \end{bmatrix} \end{array}, \tag{3.69}$$

where $r = \mu_z(+\infty)/\hbar$.

An initial state $\rho_{in} = e^{-\beta L^2 - \lambda_0}$ evolves into ρ_{out} such that at $t \to \infty$, $\ln\rho_{out}$ is a linear combination of all six operators. To see this, one needs to inspect the column L^2. None of the entries therein are zero, except for that on row I. Hence, [cf. Eq. (3.69)] L^2 evolves into all five dynamical operators. In contrast it should be noted that the identity operator evolves alone. The partition function is thus constant throughout the collision.

A set of constraints for finite times need be closed under commutation with all three Q's. In this case it contains 15 (as opposed to six) operators. More constraints are required to describe the system during the collision than after the collision. Analogous phenomena are quite familiar in the coupled-states formulation. It is not too infrequently the case that more states are significantly populated during than after the collision.

A different invariant set is generated by the operators L_z and $L_\pm$. The commutation relations are

$$\begin{aligned} &[L_z, Q_\pm] = \pm Q_\pm; \quad [L_z, Q_z] = 0\,, \\ &[L_\pm, Q_\mp] = \pm 2Q_z; \quad [L_\pm, Q_z] = \mp Q_\pm\,, \\ &[L_+, Q_+] = [L_-, Q_-] = 0\,, \\ &[L_+, L_-] = 2L_z; \quad [L_z, L_\pm] = \pm L_\pm\,. \end{aligned} \tag{3.70}$$

These show that the set of six operators $L_z, L_\pm, Q_z, Q_\pm$ is not only closed but is also an algebra.

The commutation relations, Eq. (3.70) identify the Lie algebra above as the algebra of the Euclidean group[42] $E(3)$ in three-dimensional space. This is the group of transformations corresponding to a rotation about a fixed point followed by a translation. (The group is discussed in detail in Appendix B.) The dynamical group for dipole excitation (Q_z, Q_+, Q_-) is a subgroup of $E(3)$ and is simply the group of translations in ordinary space. In order to discuss excitation of a symmetric top (rather than just a rotor) it is more convenient however to work with the six-operator $E(3)$ group. (Explicit results are provided in Appendix B.) The reason is that all irreducible unitary representations of $E(3)$ are characterized[42,50] by a pair of real numbers (p, K), where $2K$ is integer. We shall come (Appendix B) to identify K as the K quantum number of the top (which is the projection of the angular momentum along the symmetry axis of the top). $K = 0$ for the rotor. p is the intrinsic dipole moment of the top along its symmetry axis. Thus, for the case of dipole excitation the mathematician's notation is tailor made for the intended physical application.

K. Scattering matrix for dipole excitation of a rotor

We examine the properties of the scattering matrix regarding it as the $(p, K = 0)$ representation[42,49] of the Euclidean group $E(3)$. The more general case, rotational excitation of a symmetric top, is

discussed in Appendix B. The bases for the representation are the eigenvectors for the symmetric top (i.e., [51] $|KLM\rangle$) for $K=0$, which are simply the spherical harmonics (i.e., [51] $|LM\rangle$). The scattering operator is given by [cf. Eqs. (3.60) and (3.63)]

$$S=\exp[-(i/\hbar)\mu_z(\infty,-\infty)Q_z]$$
$$=\exp(-irQ_z), \tag{3.71}$$

$r=\mu_z(\infty,-\infty)/\hbar$, i.e., it is an element of the translation group in three dimensions corresponding to a translation along the z axis. $Q_z=p\cos\theta$ where as before p is the intrinsic dipole moment and θ is the angle between the dipole and the apex line of the trajectory. The matrix element $\langle L'M'|S|LM\rangle$ is nonvanishing only for $M'=M$ {a translation cannot change the projection of L, i.e., [cf. Eq. (3.70)], L_z and Q_z commute}. Hence we can define a function $J_{L',L,M}(pr)$ by

$$J_{L',L,M}(pr)=\langle L'M|e^{(-irQ_z)}|LM\rangle, \tag{3.72}$$

for L and L' non-negative integers and M an integer such that $|M|\leq L$ and L'.

The functions $J_{L',L,M}(pr)$ will be shown to be a *finite* linear combination of ordinary Bessel functions. In the mathematical literature[50] they are regarded as generalizations of the Bessel functions. The use of group-theoretic techniques to study their properties is discussed in Appendix B. Here we consider just the main results.

A generating function is obtained directly from the definition of $J_{L',L,M}$ as matrix elements of the representation of the scattering matrix

$$S|LM\rangle=\sum_{L'}J_{L',L,M}(pr)|L'M\rangle. \tag{3.73}$$

Explicitly

$$e^{-ipr\cos\theta}Y_{LM}(\theta,\phi)=\sum_{L'}J_{L',L,M}(pr)Y_{L'M}(\theta,\phi). \tag{3.74}$$

Substituting $t=\cos\theta$, $x=pr$

$$\left(\frac{(2L+1)(L-M)!}{(L+M)!}\right)^{1/2}e^{(-ixt)}P_L^M(t)$$
$$=\sum_{L'=|m|}^{\infty}\left(\frac{(2L'+1)(L'-M)!}{(L'+M)!}\right)^{1/2}J_{L',L,M}(x)P_{L'}^M(t). \tag{3.75}$$

An integral representation is immediately available from the observation [cf. Eq. (3.74)] that $J_{L',L,M}$ is just the matrix element of a plane wave between two spherical harmonics

$$J_{L',L,M}(x)=A_{L'LM}\int_{-1}^{1}dz\,e^{(-ixz)}P_{L'}^M(z)P_L^M(z). \tag{3.76}$$

Here

$$A_{L'LM}=\frac{1}{2}\left(\frac{(2L+1)(2L'+1)(L-M)!\,(L-M'!)}{(L+M)!\,(L+M')!}\right)^{1/2} \tag{3.77}$$

and $P_L^M(z)$ are the associated Legendre functions. The symmetry properties

$$J_{L',L,M}(x)=J^*_{L,L',M}(-x)$$

and

$$J_{L',L,M}(x)=J_{L,L',M}(x), \tag{3.78}$$

are evident from this representation.

An explicit expression is derived in Appendix B leading to a *finite* series representation

$$J_{L',L,M}(x)=B_{L'LM}\sum_l(-i)^l(2l+1)\begin{pmatrix}L' & l & L\\ 0 & 0 & 0\end{pmatrix}$$
$$\times\begin{pmatrix}L' & l & L\\ M & 0 & -M\end{pmatrix}j_l(x). \tag{3.79}$$

Here

$$B_{L'LM}=(-1)^M[(2L+1)(2L'+1)]^{1/2}, \tag{3.80}$$

and $j_l(x)$ is the spherical Bessel function of the first kind. The summation in Eq. (3.79) is finite for the first 3-j symbol[51] restricts the summation over l to the "triangular" condition

$$|L-L'|\leq l\leq L+L'. \tag{3.81}$$

Furthermore,

$$l+L+L'=\text{even number}.$$

Special limits of Eq. (3.79) include, in particular, a rather simple result for excitation of a rotor initially in the ground state

$$J_{L,0,0}=(-i)^l(2L+1)^{1/2}j_L(x). \tag{3.82}$$

The expected[9,52] proportionality between the transition probability ($|J_{L,0,0}|^2$) and the final volume in phase space ($2L+1$, since the relative motion is treated as a time-dependent force) is very evident in Eq. (3.82).

IV. DYNAMICAL GROUP

The purpose of this section is twofold. First, invoking the concept of the dynamical algebra, we introduce the dynamical group. This makes it possible to solve for the time evolution operator of the whole family of similar processes in one go. The different members of the family differ in the values of the parameters in the evolution operator but the algebraic form will be the same for any initial state whatever.[53] We then show that the G matrix, for the common set of constraints of similar reactions, can be similarly determined

for the entire family.

The second purpose of the section is to examine the asymptotic ($t \to \infty$) limit. This is done by using the interaction picture. We find the $\underline{G}$ matrix can be factored, $\underline{G} = \underline{G}^0 \underline{G}^I$, where $\underline{G}^I$ has a well-defined asymptotic limit. $\underline{G}^I$ is then identified as the $\underline{G}$ matrix in the interaction picture.

A. The evolution operator as an element of the dynamical group

The resolution of the Hamiltonian $H = \sum h_n(t) H_n$ was used, in Sec. II G to introduce the concept of the dynamical algebra, as the Lie algebra generated by the operators H_n [cf. Eq. (2.39)]. Integrating the equation of motion for the evolution operator in the vicinity of $U(t_0, t_0) = I$, we find

$$U(t_0 + \delta t, t_0) = I - \left(\frac{i\delta t}{\hbar}\right) \sum_n h_n(t_0) H_n + O(\delta t^2). \quad (4.1)$$

It follows that the elements of the dynamical algebra (i.e., the operators H_n) can be considered as generators of a dynamical (Lie) group. The group property

$$U(t, t_0) = U(t, t') U(t', t_0) \quad (4.2)$$

implies that $U(t_0 + \Delta t, t_0)$ is an element of the group and hence, as shown originally by Lie[54, 55] may be parametrized in the canonical form

$$U(t, t_0) = \exp\left[-\left(\frac{i}{\hbar}\right) \sum_n u_n(t, t_0) H_n\right], \quad (4.3)$$

at least in the neighborhood of the identity [$U(t_0, t_0) = I, u_n(t_0, t_0) = 0$, i.e., for u_n's that are not too large]. It will become clear that one can use the parametrization, Eq. (4.3), to considerable advantage without having to specify the magnitude of the coefficients $u_n(t, t_0)$. The final results of such manipulations will be functions whose arguments are the coefficients u_n. For this reason the $u_n(t, t_0)$ are termed "the group parameters." Specifically, they are the group parameters of the canonical form.

The important result for the purpose of analysis is the "fundamental theorem" of Lie[54, 55] that the (dynamical) algebra determines the (dynamical) group. A family of similar reactions will thus have the same dynamical group. We shall shortly demonstrate that this implies that the $\underline{G}$ matrix, regarded as a function of the group parameters, will be identical for all members of the family. A single $\underline{G}$ matrix will suffice to characterize the evolution for an entire family of reactions. Moreover, the determination of $\underline{G}$ as a function of the group parameters requires only algebraic operations. As is perhaps already obvious from Eq. (4.3), the scattering matrix elements for different reactions of the same family will also be the same (analytic) function of the group parameters.

Different reactions of the same family (i.e., same dynamic algebra) can differ only in the value of the group parameters. Explicit nonlinear differential equations for the coefficients $u_n(t, t_0)$ (the group parameters) will be derived in Sec. V E. We have found these equations to be quite practical particularly so when (cf. Sec. V G) the dynamic algebra is solvable. There always is the optional alternative of using an iterative procedure to determine the u_n's as discussed by Magnus.[56] Finally, as a last resort, numerical methods can be used since, at least for small u_n's. Magnus has proved that the solution exists. It should be stressed however that the values of the group parameters are not required for determining the analytic form of the $\underline{G}$ or $\underline{S}$ matrices. They are only required if one wants to predict the value of the matrix elements involved.

An alternative,[57] "product form" representation,

$$U(t, t_0) = \prod_n \exp\left[-\left(\frac{i}{\hbar}\right) \mu_n(t, t_0) H_n\right], \quad (4.4)$$

has been explored by Norman and Wei.[58] They have also shown that the representation is global [i.e., also valid far from $U(t_0, t_0)$] for all solvable Lie algebras. The product form representation can be arranged to yield very many different parametrizations for U. For example, the terms in the product can be taken in different orders or some operators H_n can appear more than once[59] in Eq. (4.4), etc.

The product form representation has more flexibility and is often more useful in practice.

B. $\underline{G}$ matrix for similar collisions

The construction of the $\underline{G}$ matrix for a particular Hamiltonian was discussed in Sec. II F. Here we consider the determination of a functional form for $\underline{G}$ that is common to all processes with the same dynamical algebra. The only difference in the $\underline{G}$ matrices for similar collisions will be in the values of the parameters.

The construction is straightforward and will also serve to prove a result which will be derived in Sec. V D on more formal grounds: the $\underline{G}$ matrix is a representation of the dynamical group.

Let the evolution operator define an operator A by $U = e^A$. Since A can be written as a linear combination of elements of the dynamical algebra

$$A = -\left(\frac{i}{\hbar}\right) \sum_n u_n(t, t_0) H_n, \quad (4.5)$$

we can use the $\underline{d}(H_n)$ matrices, introduced in Eq. (2.36), to define $\underline{d}(A)$ by

$$[A, A_s] = \sum_t d_{ts}(A) A_t , \tag{4.6}$$

so that

$$\underline{d}(A) = -\left(\frac{i}{\hbar}\right) \sum_n u_n(t, t_0) \underline{d}(H_n) . \tag{4.7}$$

Consider now the more general form $U(x) = e^{xA}$ and an associated matrix $\underline{G}(x)$, i.e., for any constraint A_r,

$$U(x) A_r U^\dagger(x) \equiv e^{xA} A_r e^{-xA} = \sum_s A_s G_{sr}(x) . \tag{4.8}$$

Our aim is to derive a differential equation for $G(x)$ and to obtain the required matrix G as the solution $G(x)$ at $x = 1$. Taking the derivative with respect x of both sides of Eq. (4.8)

$$\sum_s A_s \frac{\partial G_{sr}(x)}{\partial x} = [A, U(x) A_r U^\dagger(x)] = \sum_s G_{sr} [A, A_s] = \sum_t \sum_s G_{sr} d_{ts}(A) A_t = \sum_s \left(\sum_t G_{tr} d_{st} \right) A_s , \tag{4.9}$$

where [cf. Eq. (4.7)] $\underline{d}(A)$ is independent of x. Since the constraints are linearly independent

$$\frac{\partial G_{sr}(x)}{\partial x} = \sum_t d_{st}(A) G_{tr}(x) \tag{4.10}$$

or

$$\frac{\partial \underline{G}(x)}{\partial x} = \underline{d}(A) \underline{G}(x) , \tag{4.11}$$

with $\underline{G}(x = 0) = \underline{I}$. Now $\underline{d}(A)$ is a constant matrix so the solution of Eq. (4.11) is immediate, $\underline{G}(x) = e^{x\underline{d}(A)}$. Introducing the explicit expression for $\underline{d}(A)$ from Eq. (4.7) we have for $\underline{G} \equiv \underline{G}(x = 1)$

$$\underline{G} = \exp\left[-\left(\frac{i}{\hbar}\right) \sum_n u_n(t, t_0) \underline{d}(H_n) \right] . \tag{4.12}$$

Here the matrices $\underline{d}(H_n)$ [cf. Eq. (2.36)],

$$[H_n, A_r] = \sum_s d_{sr}(H_n) A_s , \tag{4.13}$$

are common to all similar reactions and are time independent. The only dependence on the parameters $h_n(t)$ of the Hamiltonian is through (time-dependent) group parameters u_n of the evolution operator. Had we used a different representation for U, say the product form, Eq. (4.14), then the parametrization of G would change accordingly. For the product form Eq. (4.14),

$$\underline{G} = \prod_n \exp\left[-\left(\frac{i}{\hbar}\right) \mu_n(t, t_0) \underline{d}(H_n) \right] . \tag{4.14}$$

Again we note that, if so desired, an operator H_n may appear more than once in the product[59] and that the order of terms is a matter of convenience.

To obtain explicit results for elements of G it is still necessary to evaluate the exponentials in Eqs. (4.12) or (4.14). This need be done only once for all processes with the same dynamical algebra. A more pedestrian route is to use the Baker-Hausdorff expansion, Eq. (3.20), with $U = e^A$. In principle this will generate all the elements of the matrix G by expanding $UA_rU^\dagger$ for all the constraints A_r. An example was provided in Sec. III E. In Sec. V F we shall show that Eqs. (4.12) or (4.14) provide a practical route also for the determination of the inverse, G^{-1} matrix required to obtain the mean value of the constraints as a function of time, Eq. (2.28). Once G is known as a function of the group parameters, obtaining G^{-1} reduces to a trivial operation.

C. G matrix in the interaction picture

As in other formulations of collision theory, the interaction picture is introduced to factor out the oscillatory time dependence due to evolution under the unperturbed Hamiltonian H_0. Thus, with $\rho(t)$ as the density operator in the Schrödinger picture, one puts $[U_0 \equiv U_0(t, 0)]$.

$$\rho(t) = U_0 \rho^I(t) U_0^\dagger . \tag{4.15}$$

Since $U_0(t, 0)$ is the evolution operator (from 0 to t) under the Hamiltonian H_0, Eq. (4.15) has the interpretation that $\rho^I(t)$ is the Schrödinger picture density operator which, under the unperturbed time evolution from 0 to t, would evolve to $\rho(t)$. Since $\rho(t) = U\rho(0)U^\dagger$, the evolution operator in the interaction picture, U_I, $\rho^I(t) = U_I \rho^I(0) U_I^\dagger$ satisfies $U = U_0 U_I$. That $\rho^I(t)$ does have well-defined asymptotic limits is suggested by the equations of motion in the interaction picture,

$$i\hbar \frac{\partial U_I}{\partial t} = V_I(t) U_I , \quad i\hbar \frac{\partial \rho^I}{\partial t} = [V_I(t), \rho^I] . \tag{4.16}$$

Here $V_I(t)$,

$$V_I(t) = U_0^\dagger(t, 0) V(t) U_0(t, 0) , \tag{4.17}$$

is the potential in the interaction picture. When the time dependence of $V(t)$ is due to a classical description of the relative motion it is clear that $V_I(t) \to 0$ as $t \to \infty$ and the equations of motion will manifestly imply that U_I and ρ^I will tend to a constant limit. Otherwise one will need to appeal, as usual,[24,25] to the adiabatic switching procedure.

Equations (4.16) have the same form as the corresponding equations in the Schrödinger picture with $V_I(t)$ as the "Hamiltonian." The discussion

of Sec. II G can thus be adapted to the interaction picture by defining the dynamical constraints in the interaction picture as the set of operators closed under commutation with $V_I(t)$,

$$[V_I(t), A_r] = \sum_s \alpha^I_{sr}(t) A_s . \tag{4.18}$$

By taking the operators A_s to be time independent (i.e., the A_s are operators in the Schrödinger picture) one can ensure (as in Sec. II F) that similar reactions will have a common set of constraints. The corresponding matrix $\underline{G}$ in the interaction picture is introduced [cf. Eq. (2.30)] by

$$U_I(t, t_0) A_r U_I^\dagger(t, t_0) = \sum_s A_s G^I_{sr}(t, t_0) . \tag{4.19}$$

The relation of G to G^I follows provided that the set $\{A_r\}$ is closed under commutation with $H(t)$ as well (so that G can be defined). Then [with $U \equiv U(t, t_0)$, etc.],

$$\begin{aligned} UA_r U^\dagger = U_0 U_I A_r U_I^\dagger U_0^\dagger &= \sum_s G_{sr} A_s \\ &= U_0 \sum_t G^I_{tr} A_t U_0^\dagger \\ &= \sum_{s,t} G^0_{st} G^I_{tr} A_s , \end{aligned} \tag{4.20}$$

or

$$\underline{G} = \underline{G^0}\,\underline{G^I} . \tag{4.21}$$

Here G^0 is the G matrix for evolution under H_0,

$$U_0 A_t U_0^\dagger = \sum_s G^0_{st} A_s , \tag{4.22}$$

and can be factored out of the G matrix, leaving behind a matrix $\underline{G^I} \equiv \underline{G^I}(t, t_0)$ which depends on time only due to the interaction,

$$i\hbar \frac{\partial \underline{G^I}(t, t_0)}{\partial t} = \underline{\alpha^I}(t)\,\underline{G^I}(t, t_0), \quad \underline{G^I}(t_0, t_0) = \underline{I} , \tag{4.23}$$

and with a well-defined asymptotic behavior [$\underline{\alpha^I}(t)$ vanishes for $t \to \pm\infty$].

The well-defined limit of $\underline{G^I}(t, 0)$ as $t \to -\infty$ and the corresponding well-defined limit of $\underline{G^I}(0, t_0)$ as $t_0 \to -\infty$ imply, using the group property that $\underline{G^I}(+\infty, -\infty)$,

$$\underline{G^I}(+\infty, -\infty) = \underline{G^I}(+\infty, 0)\,\underline{G^I}(0, -\infty) , \tag{4.24}$$

is similarly well defined.

D. Lagrange parameters in the interaction picture

Introducing the Lagrange parameters $\lambda^I_r(t)$ conjugate to the set of constraints A_r, we can write the density operator as

$$\ln \rho^I(t) = -\sum_{r=0} \lambda^I_r(t) A_r , \tag{4.25}$$

or, using Eq. (4.19) and the fact that $\ln \rho^I(t)$ is a solution of the Liouville equation in the interaction picture

$$\underline{\lambda^I}(t) = \underline{G^I}\,\underline{\lambda^I}(t_0) . \tag{4.26}$$

The "interaction" Lagrange parameters correspond to a density operator of maximal entropy subject to the specified values of $\mathrm{Tr}\{\rho^I(t) A_r\}$.

It should however be noted that A_r is an operator in the Schrödinger picture. Hence $\mathrm{Tr}\{\rho^I(t) A_r\}$ is not the expectation value of A_r at the time t. The proper interpretation is provided by Eq. (4.15), $\rho^I(t) = U_0^\dagger(t, 0) \rho(t) U_0(t, 0)$. In words, $\rho^I(t)$ can be regarded as a Schrödinger picture density operator with the following history: First the system evolved forward in time, under the action of the full Hamiltonian. This leads to the density operator $\rho(t)$. Then the system evolved backwards in time, from time t to time 0, under the action of H_0. The resulting density operator is $\rho^I(t)$. Note however that since H_0 does not (by definition) induce transitions $\rho(t)$ and $\rho^I(t)$ correspond to the same distribution of states. $\mathrm{Tr}\{\rho^I(t) A_r\}$ is thus the expectation value of A_r for the system with the time evolution as described above. One can, of course, introduce $A^I_r(t)$, the operator A_r in the interaction picture $A^I_r(t) = U_0^\dagger A_r U_0$. It follows from Eqs. (4.15) and (4.21) that

$$\ln \rho^I(t) = -\sum_{r=0} \lambda_r(t) A^I_r(t) . \tag{4.27}$$

Here the λ_r's are the same as in the Schrödinger picture, Eq. (2.11), since they are conjugate to the $\langle A_r \rangle(t)$'s and $\mathrm{Tr}\{\rho^I(t) A^I_r(t)\} = \mathrm{Tr}\{\rho(t) A_r\}$.

The relation of the λ^I's to the λ's obtained (Sec. II) in the Schrödinger picture can be determined provided the set $\{A_r\}$ is also closed under commutation with H so that it suffices to characterize also the evoluting under H_0. Then

$$\begin{aligned} \sum_r \lambda_r(t) A_r = \ln \rho(t) = U_0 \ln \rho^I(t) U_0^\dagger &= \sum_s \lambda^I_s(t) U_0 A_s U_0^\dagger \\ &= \sum_r A_r \sum_s G^0_{rs} \lambda^I_s(t) \end{aligned} \tag{4.28}$$

or

$$\underline{\lambda}(t) = \underline{G^0}\,\underline{\lambda^I}(t) . \tag{4.29}$$

The advantage of the interaction picture in factoring out the evolution under H_0 is again evident. By requesting, as usual, that the Schrödinger and interaction pictures be identical at some value of t, here, $t = 0$, so that $\lambda^I(0) = \lambda(0)$ one readily verifies that Eqs. (4.26) and (4.29) are consistent with the result $\underline{\lambda}(t) = \underline{G}\,\underline{\lambda}(t_0)$.

The canonical [cf. Eq. (4.3)] and product [cf. Eq. (4.4)] forms for the evolution operator and the $\underline{G}$ matrix are equally valid in the interaction picture. A dynamical algebra for a family of similar collisions is obtained by putting

$$V_I(t)=\sum_n v_n(t)V_n\,, \tag{4.30}$$

where the V_n's are time independent and are enlarged so as to close an algebra. Then,

$$U_I=\exp\left[-\left(\frac{i}{\hbar}\right)\sum_n u_n^I(t,t_0)V_n\right]\,,$$

and (4.31)

$$\underline{G}_I=\exp\left[-\left(\frac{i}{\hbar}\right)\sum_n u_n^I(t,t_0)\underline{d}(V_n)\right]\,.$$

E. Asymptotic limits of the density operators

The analysis of collision experiments requires the limiting form of the density operator after the collision. As in formal time-dependent collision theory[24,25] we can obtain this limit as follows. Let the collision run its course until such time t ($t\to\infty$) that the interaction has decreased to zero. We then bring the system back for inspection at some finite time, say $t=0$. In order that the backwards time evolution not cause any transitions (i.e., in order that the final-state distribution is the same at t and 0), we travel back under H_0. The resulting state at 0 is

$$\begin{aligned}\rho_{\text{out}}&=\lim_{t\to\infty}U_0^\dagger(t,0)\rho(t)U_0(t,0)\\&=\lim_{t\to\infty}U_0^\dagger(t,0)U(t,0)\rho(0)U^\dagger(t,0)U_0(t,0)\\&=\lim_{t\to\infty}U_I(t,0)\rho(0)U_I^\dagger(t,0)\,.\end{aligned} \tag{4.32}$$

Here $\rho(t)$ is the density operator in the Schrödinger picture and if we take $\rho^I(0)\equiv\rho(0)$,

$$\rho_{\text{out}}=\lim_{t\to\infty}U_I(t,0)\rho^I(0)U_I^\dagger(t,0)=\lim_{t\to\infty}\rho^I(t)\,. \tag{4.33}$$

By a similar reasoning we take the $t\to-\infty$ limit by bringing the system from $-\infty$ to $t=0$ under the action of H_0. Then

$$\rho_{\text{in}}=\lim_{t\to-\infty}U_0(0,t)\rho(t)U_0^\dagger(0,t)=\lim_{t\to-\infty}\rho^I(t)\,. \tag{4.34}$$

The "in" and "out" states are simply the limits of the density operators (in the interaction picture) before and after the collision. It is for this reason that it is sufficient to construct the set of constraints as being closed under $V_I(t)$. The time evolution under H_0 is irrelevant to a scattering experiment which seeks to determine the transitions by the potential.

The scattering event is thus represented by[24]

$$\rho_{\text{out}}=S\rho_{\text{in}}S^\dagger \tag{4.35}$$

or

$$\ln\rho_{\text{out}}=S\ln\rho_{\text{in}}S^\dagger\,,$$

where the scattering operator is given, as usual, by

$$S=\lim_{t\to\infty}\lim_{t'\to-\infty}U_I(t,t')\,. \tag{4.36}$$

If the initial state is pure, one can also introduce ψ_{in} and ψ_{out} such that[24,25]

$$\psi_{\text{out}}=S\psi_{\text{in}}\,. \tag{4.37}$$

V. REPRESENTATIONS OF THE DYNAMICAL GROUP

Viewing the solution of the equations of motion as the determination of a representation of the dynamical group has both practical and conceptual advantages. On the practical side it offers the possibility of obtaining closed expressions for the elements of the scattering matrix or for the density matrix. This aspect is already evident in Sec. III [see Eqs. (3.41), (3.45), or (3.72)]. Additional applications to more complex Hamiltonians have been worked out and are in preparation for publication. In this section we shall be primarily concerned with this point of view as means of directing attention to the similarity and the difference of the present method as compared with the usual formulation of collision theory. We shall conclude that both approaches seek a representation of the dynamical group. In focusing attention on the G matrix one seeks a representation in a (finite-dimensional) basis provided by the constraints (which are, of course, operators) whereas in the usual method one seeks a representation in a Hilbert space of state vectors. In addition, the concept of a representation of a group enables one to introduce the group parameters, a concept which is useful for both types of representations.

A. Scattering matrix as a unitary representation of a Lie group

In the basis of eigenstates of H_0, say $|m\rangle$, the scattering matrix is defined, as usual, by

$$S|n\rangle=\sum_m|m\rangle S_{mn}\,, \tag{5.1}$$

where S is the scattering operator [cf. Eq. (4.35)] which induces the transformation of "in" to "out" states. In terms of the operators in the dynamical algebra [cf. Eq. (4.3)]

$$S=\exp\left[-\left(\frac{i}{\hbar}\right)\sum_n s_n V_n\right]\,, \tag{5.2}$$

where $s_n=u_n^I(+\infty,-\infty)$ and the operator V_n are common to a family of similar reactions. The

magnitudes of the numerical coefficients s_n can be determined using the methods in Sec. V E. In terms of the product form for U_I, Eq. (4.4),

$$S = \prod_n e^{-(i/\hbar)\sigma_n V_n}, \tag{5.3}$$

where $\sigma_n = \mu_n^I(\infty, -\infty)$.

The scattering operator is thus an element of the dynamical group (in the interaction picture). If the unitary representation of the group (which is generated by the dynamical algebra) is known in the literature[55] one can obtain the S matrix explicitly. It is, of course, necessary to verify that the basis used in the literature is that of eigenfunctions of H_0. It can be checked by examining the operation of the elements of the dynamical algebra on the basis functions. (This check will also serve to identify the desired representation, as was explicitly shown in Sec. III G.) Simple applications of this method were already noted. Additional technical procedures which simplify the task of obtaining a representation are discussed in Appendix B. Even when an explicit representation is not available in the literature the group-theoretic point of view is useful in ensuring that the matrix elements of $\underline{S}$ are analytic functions of the group parameters (i.e., the s_n's or the σ_n's) and in generating relations between the different elements (recursion relations, addition formulas, sum rules, etc.; examples are given in Appendix B).

B. Density matrix as a representation of a complex Lie group

It was possible to regard the scattering matrix as a representation of a real Lie group because (i) the group is generated by elements of a Lie algebra [cf. Eq. (4.1)], and (ii) if we write $U = e^A$, then A is necessarily an anti-Hermitian operator and the commutator of two anti-Hermitian operators is, itself, an anti-Hermitian operator. As things stand, neither condition obtains for ρ.

To begin with, ρ is defined in terms of the set of constraints: a set of operators A_r which are closed under commutation with $V_I(t)$. This invariant set is not necessarily an algebra. If however we now enlarge the set so that it does form an algebra, then the use of the Jacobi identity [cf. Eq. (2.40)] readily shows that all elements of the algebra are invariant under commutation with $V_I(t)$. Condition (i) is now satisfied. The (enlarged) set of constraints form an algebra.

When we put $\rho = \exp(-\sum\lambda_r A_r)$ then $\sum\lambda_r A_r$ need be Hermitian. The commutator of two Hermitian operators is anti-Hermitian. ρ cannot be regarded as an element of a real Lie group. It can however be regarded as an element of a complex Lie group provided we regard the λ_r's as complex numbers (even when the A_r's are Hermitian).

One can thus regard the density matrix $\underline{\rho}$

$$\underline{\rho}|n\rangle = \sum_m |m\rangle \rho_{mn}, \tag{5.4}$$

as a representation of a complex Lie group. The density matrix elements will now be analytic functions of the Lagrange multipliers which are the group parameters. Of course, we are only interested in the representation of those elements of the complex Lie group for which $\sum\lambda_r A_r$ is Hermitian (i.e., for which ρ is Hermitian).

Thus far we have dealt with representations using state vectors as a basis, i.e., representations in a Hilbert space. We turn now to lower dimensional representations.

C. Constraints as a basis for the representation of the dynamical algebra

The elements $\{V_m\}$ of the dynamical algebra (in the interaction picture) are said to be represented by the set of matrices $\{\underline{d}(V_m)\}$ if the matrices satisfy the same commutation relations as the elements of the algebra. It is thus required that $[V_m, V_n]$ be represented by $\underline{d}(V_m)\underline{d}(V_n) - \underline{d}(V_n)\underline{d}(V_m)$. If one now defines $\underline{d}(V_m)$ via the condition that the constraints form a closed set under commutation with the elements of the dynamical algebra, [cf. Eq. (2.36)]

$$[V_m, A_r] = \sum_s d_{sr}(V_m) A_s, \tag{5.5}$$

it follows, on using the Jacobi identity [cf. Eqs. (2.40) or (5.8) below], that the required condition does obtain. We thus have one more interpretation of the constraints: the (closed) set of constraints provides a basis for a representation of the dynamical algebra.

To center attention on this interpretation of the constraints it is convenient to define the (linear) operator adV_m by[36] [cf. Eq. (3.21)]

$$(adV_m)A_r \equiv [V_m, A_r] = \sum_s d_{sr}(V_m) A_s. \tag{5.6}$$

The Jacobi identity then implies that (adV_m) has the same commutation relations as the dynamical algebra itself. Explicitly

$$\begin{aligned}(adV_m adV_n - adV_n adV_m)A_r &= [V_m, [V_n, A_r]] - [V_n, [V_m, A_r]] \\ &= [[V_m, V_n], A_r] = (ad[V_m, V_n])A_r,\end{aligned} \tag{5.7}$$

or, in a formal fashion

$$[adV_m, adV_n] = ad[V_m, V_n]. \tag{5.8}$$

It is for this reason that the representation via the

$\underline{d}$ matrices is sometimes known as the adjoint representation.

D. $\underline{G}$ matrix as a representation of the dynamical group

The essential point of Sec. II was that the set of constraints, determined as the set closed under commutation with H, will be closed also under time evolution. In Lie algebraic terms this is simply the result that any representation of the algebra induces a representation of the group. Indeed, we have already invoked the group property, Eq. (4.24) of the $\underline{G}$ matrix.

In formal terms we note that one can introduce powers of adV_n, e.g., $(adV_n)^2 A_r = [V_n, [V_n, A_r]]$, so that [cf. Eq. (3.20)] $e^{V_n} A_r e^{-V_n} = e^{(adV_n)} A_r$. Hence

$$U_I A_r U_I^\dagger \equiv \exp\left[-\left(\frac{i}{\hbar}\right)\sum_n u_n (adV_n)\right] A_r = \sum_s A_s G^I_{sr}. \tag{5.9}$$

The result [cf. Eq. (4.12)]

$$\underline{G}^I = \exp\left[-\left(\frac{i}{\hbar}\right)\sum_n u_n \underline{d}(V_n)\right] \tag{5.10}$$

can now be viewed as an immediate consequence of Eqs. (5.6) and (5.9).

E. Equations of motion for the dynamical group parameters

This section is an exercise in the application of the concept of representations aimed at obtaining equations of motion for the parameters [u_n, cf. Eq. (4.3); μ_n, cf. Eq. (4.4)] of the dynamical group.

Consider first Eq. (3.20) which implies that

$$e^{(adA)} A = A. \tag{5.11}$$

Taking A to be defined by $U = e^{(A)}$ we note that A is represented by a vector whose components are the group parameters. Similarly e^{adA} is represented by $\underline{G}$. Hence the representation of Eq. (5.11) is

$$\underline{G}(t, t_0)\underline{u}(t, t_0) = \underline{u}(t, t_0). \tag{5.12}$$

It follows from Eq. (5.12) that if we choose the initial state such that $\underline{\lambda}(t_0) = \underline{u}(t, t_0)$ then $\underline{\lambda}(t) = \underline{G}(t, t_0)\underline{\lambda}(t_0) = \underline{\lambda}(t_0)$. The initial state so chosen will evolve from t_0 to t in such a manner that at time t (but not necessarily before or after that time) it will assume its precise initial form.

To obtain equations of motion for the group parameters we write the equation of motion of $U^\dagger$, $-i\hbar \partial U_I^\dagger/\partial t = U_I^\dagger V_I(t)$ as

$$i\hbar U_I \left(\frac{\partial U_I^\dagger}{\partial t}\right) = -V_I(t), \tag{5.13}$$

or, if $U_I = e^A$,

$$e^A \frac{i\hbar\partial}{\partial t} e^{-A} \equiv e^{adA} \frac{i\hbar\partial}{\partial t} = -V_I. \tag{5.14}$$

To perform the operations in Eq. (5.14) we use the identity (Appendix C)

$$e^A \frac{i\hbar\partial}{\partial t} e^{-A} \equiv e^{adA} \frac{i\hbar\partial}{\partial t} = \int_0^1 dx\, e^{xadA} \frac{-i\hbar\partial A}{\partial t} = \phi(adA) \frac{-i\hbar\partial A}{\partial t}, \tag{5.15}$$

where (cf. Appendix C) $\phi(z) = (e^z - 1)/z = \sum z^{n-1}/n!$

The representation of the awesome identity is quite innocent. e^{xadA} is represented by $\underline{G}(x\underline{u})$, where the argument in G serves to indicate that all group parameters are to be multipled by x. $i\hbar\partial A/\partial t$ is represented by $\partial u(t, t_0)/\partial t$, and $V_I(t)$ is represented by $\underline{v}(t)$ [i.e., $V_I(t) = \sum v_n(t) V_n$]. Hence Eqs. (5.14) and (5.15) read

$$\int_0^1 \underline{G}(x\underline{u}) \frac{\partial \underline{u}}{\partial t} = \underline{v}(t) \tag{5.16}$$

or

$$\phi(\underline{d}(A)) \frac{\partial \underline{u}}{\partial t} = \underline{v}(t), \tag{5.17}$$

with the boundary condition $\underline{u}(t_0, t_0) = \underline{0}$. One now has a choice of solving either of the (equivalent) Eqs. (5.16) or (5.17). An illustration of the solution of Eq. (5.16) was provided in Sec. III. Here we examine Eq. (5.17). $\phi(z)$ has an inverse,

$$\phi^{-1}(z) = \frac{z}{(e^z - 1)} = \sum_{k=0} \frac{B_k}{k!} z^k, \tag{5.18}$$

where B_k's are the Bernoulli numbers. Hence

$$\frac{\partial \underline{u}(t, t_0)}{\partial t} = \phi^{-1}[\underline{d}(A)]\underline{v}(t) = \sum_{k=0} \frac{B_k}{k!} \underline{d}^k(A)\underline{v}(t). \tag{5.19}$$

If the algebra is nilpotent [which means that $\underline{d}^n(A) = 0$ for all $n \geq n_0 > 0$], the form, Eq. (5.19), is quite suitable for practical work.

As an exercise the reader may wish to show the equivalence of Eqs. (5.16) or (5.17) to the equation for $\partial \underline{u}/\partial t$ obtained by taking the time derivative of both sides of Eq. (5.12).

An alternative use of $\underline{G}^I$ as a representation of U_I [cf. Eq. (5.9)] is in the derivation of equations of motion for the group parameters in the product form, Eq. (4.4), for the evolution operator,

$$U_I = \prod_{r=1}^N U_r; \quad U_r(t, t_0) = \exp\left[-\left(\frac{i}{\hbar}\right)\mu_r(t, t_0) V_r\right], \tag{5.20}$$

$$i\hbar \frac{\partial U_r}{\partial t} = \frac{\partial \mu_r}{\partial t} V_r U_r. \tag{5.21}$$

Hence

$$i\hbar \frac{\partial U_I}{\partial t} = \sum_{r=1}^N \frac{\partial \mu_r}{\partial t} \left(\prod_{k=1}^{r-1} U_k\right) V_r \left(\prod_{l=r+1}^N U_l\right), \tag{5.22}$$

so that[58]

$$i\hbar \frac{\partial U_I}{\partial t} U_I^\dagger = \sum_{r=1}^{N} \frac{\partial \mu_r}{\partial t} \left(\prod_{l=1}^{r-1} U_l \right) V_r \left(\prod_{l=r-1}^{1} U_l^\dagger \right)$$

$$= V_I(t) = \sum_s v_s(t) V_s . \qquad (5.23)$$

Obtaining the representation of Eq. (5.23) is immediate, if we define $G(\mu_1, \ldots, \mu_N)$ as the representation matrix when U is in the product form

$$\left(\prod_{l=1}^{r-1} U_l \right) V_r \left(\prod_{l=r-1}^{1} U_l^\dagger \right)$$

$$= \sum_s G_{sr}(\mu_1, \mu_2, \ldots, \mu_{r-1}, 0, \ldots, 0) V_s$$

$$= \sum_s G_{sr}^{(r-1)} V_s . \qquad (5.24)$$

$\underline{G}^{(r-1)}$, defined by the last line is simply the $\underline{G}$ matrix evaluated for $\mu_r = \mu_{r+1} = \ldots \mu_N = 0$. The representation of Eq. (5.23) is thus

$$\sum_{r=1}^{N} \frac{\partial \mu_r}{\partial t} G_{sr}^{(r-1)} = v_s(t), \quad s = 1, \ldots, N, \qquad (5.25)$$

where $\mu_r = \mu_r(t, t_0)$ with the boundary condition $\mu_r(t_0, t_0) = 0$ and where the coefficients $(G_{sr}^{(r-1)})$ are functions of the μ_r's. Equation (5.25) provides N (nonlinear) equations of motion for the group parameters. The existence of a solution is assured[58] when the dynamical algebra is solvable (Sec. V G).

F. Group property

The group property for the evolution operator $U(t, t')U(t', t_0) = U(t, t_0)$ (i.e., for the elements of the dynamical group) implies a corresponding property for the representation matrices. Explicitly

$$\underline{G}(\underline{u}(t, t'))\, \underline{G}(\underline{u}(t', t_0)) = \underline{G}(\underline{u}(t, t_0)). \qquad (5.26)$$

The vector notation $G(\underline{u})$ is simply a reminder that G is a function of the set, $\underline{u} = u_1, \ldots, u_N$, of group parameters. The set of group parameters $\underline{u}(t, t_0)$ is necessarily an analytic function of the sets $\underline{u}(t', t_0)$ and $\underline{u}(t, t')$. A particular illustration of this general conclusion is as follows.

$\underline{G}^{-1}$ is the matrix representing $U^{-1}(t, t_0)$ but $(e^A)^{-1} = e^{-A}$ and hence, with $A = -(i/\hbar)\sum u_n^I(t, t_0) V_n$,

$$U^{-1}(t, t_0) = \exp\left[-\left(\frac{i}{\hbar} \right) \sum_n [-u_n^I(t, t_0)] V_n \right], \qquad (5.27)$$

or, in terms of the (canonical) representation

$$[\underline{G}^I(\underline{u}^I(t, t_0))]^{-1} = \underline{G}^I(-\underline{u}^I(t, t^0)). \qquad (5.28)$$

If one knows $\underline{G}$ as a function of the group parameters, its inversion can be trivially executed, by inverting the sign of all the group parameters.

Since $U^{-1}(t', t_0) = U(t_0, t')$ it further follows from Eqs. (5.27) and (5.28) that

$$u_r^I(t', t_0) = -u_r^I(t_0, t') . \qquad (5.29)$$

Equation (5.29) corresponds to the general result, Eq. (5.26), for the special case $t = t_0$. It is essentially a statement of microscopic reversibility. More general relations can be worked out but are essentially an iterative solution of Eq. (5.17).

G. Solvable dynamical algebra

Considerable simplification occurs when the Lie algebra is solvable.[17,58] In practice this means that the matrices $\underline{d}$ which represent the algebra can be transformed simultaneously to a triangular form. (If the algebra is also nilpotent then there are zeros also along the diagonal.)

Taking the $\underline{d}$ matrices to have an upper triangular form (i.e., zeros for all elements below the diagonal) it follows that we can transform the basis (i.e., the constraints, cf. Sec. II I) in such a manner that the equations defining $\underline{d}$ can be brought to the form

$$\begin{aligned}
(adV_n)A_1 &= [V_n, A_1] = d_{11}A_1 , \\
(adV_n)A_2 &= [V_n, A_2] = d_{12}A_1 + d_{22}A_2 , \\
&\vdots \qquad\qquad \vdots \\
(adV_n)A_m &= [V_n, A_m] = d_{1m}A_1 + d_{2m}A_2 + \cdots + d_{mm}A_m .
\end{aligned} \qquad (5.30)$$

This form is valid for all V_n's in the algebra (when it is solvable) but the coefficients d_{ij} do depend on the particular operator $d_{ij} \equiv d_{ij}(V_n)$.

Any power of an upper triangular matrix is again an upper-triangular matrix and hence the $\underline{G}$ matrix can also be brought to an upper-triangular form by using the same basis set of operators [Eq. (5.30)] that brought the $\underline{d}$ matrices to a triangular form

$$\begin{aligned}
UA_1U^\dagger &= G_{11}A_1 , \\
UA_2U^\dagger &= G_{12}A_1 + G_{22}A_2 , \\
&\vdots \qquad\qquad \vdots \\
UA_mU^\dagger &= G_{1m}A_1 + G_{2m}A_2 + \cdots + G_{mm}A_m .
\end{aligned} \qquad (5.31)$$

A practical illustration of this general result has been previously considered.[61] Simplifications also occur in the equations for the time dependence of the group parameters, Sec. V E and in the equations for the time dependence of the Lagrange parameters. These transform in an opposite (i.e., contragradient) manner to the constraints, i.e., $\underline{\lambda}(t) = \underline{G}\underline{\lambda}(t_0)$, and hence when $\underline{G}$ is upper triangular

$$\begin{aligned}
\lambda_1(t) &= G_{11}\lambda_1(t_0) + G_{12}\lambda_2(t_0) + \cdots + G_{1m}\lambda_m(t_0) \\
\lambda_2(t) &= \qquad\quad G_{22}\lambda_2(t_0) + \cdots + G_{2m}\lambda_m(t_0) \\
&\vdots \qquad\qquad \ddots \\
\lambda_m(t) &= \qquad\qquad\qquad\quad G_{mm}\lambda_m(t_0) .
\end{aligned} \qquad (5.32)$$

When one is concerned only with the Lagrange parameters for one particular reaction it is simpler to work with the equation of motion

$$i\hbar \frac{\partial \underline{\lambda}(t)}{\partial t} = \underline{\alpha}(t)\underline{\lambda}(t) . \tag{5.33}$$

Since $\underline{\alpha}(t)$ (like $\underline{G}$) is upper triangular [compare the definition, Eq. (2.13), of $\underline{\alpha}$ with Eq. (5.30)] one can first solve directly for $\lambda_m(t)$

$$i\hbar \frac{\partial \lambda_m(t)}{\partial t} = \alpha_{mm}\lambda_m(t) , \tag{5.34}$$

then substitute the solution

$$\lambda_m(t) = \exp\left(-i \int_{t_0}^{t} \frac{\alpha_{mm}(t')dt'}{\hbar}\right) \lambda_m(t_0) \tag{5.35}$$

in the equation for λ_{m-1},

$$i\hbar \frac{\partial \lambda_{m-1}(t)}{\partial t} = \alpha_{m-1,m-1}\lambda_{m-1}(t) + \alpha_{m-1,m}\lambda_m(t) , \tag{5.36}$$

which can then be solved for the unknown λ_{m-1}. One then solves for λ_{m-2}, etc.

The equations of motion for the group parameters also simplify. Taking the product representation as an example, we transform $\underline{G}$ (cf. Sec. II I) to a lower-triangular form. In this case Eq. (5.25) reads

$$\begin{aligned} &G_{11}^{(0)} \frac{\partial \mu_1}{\partial t} = v_1(t) , \\ &G_{21}^{(0)} \frac{\partial \mu_1}{\partial t} + G_{22}^{(1)} \frac{\partial \mu_2}{\partial t} = v_2(t) , \\ &\vdots \end{aligned} \tag{5.37}$$

Here [cf. Eq. (5.24)] $G_{11}^{(0)}$ is just a constant (i.e., independent of the group parameters) so that

$$\mu_1(t, t_0) = -\left(\frac{1}{G_{11}^{(0)}}\right) \int_{t_0}^{t} v_1(\tau)\, d\tau . \tag{5.38}$$

Now that $\mu_1(t, t_0)$ is available we can obtain $G_{22}^{(1)}(\mu_1)$ and hence solve for μ_2

$$\begin{aligned} \mu_2(t, t_0) = -\int_{t_0}^{t} &[G_{22}^{(1)}(\mu_1(\tau, t_0))]^{-1} \\ &\times [v_2(\tau) - G_{21}^{(0)} G_{11}^{(0)^{-1}} v_1(\tau)]\, d\tau . \end{aligned} \tag{5.39}$$

H. Summary

In the usual formulation of quantum mechanics one has the choice of working with the equations for the state vectors or with their representations. For example, to the interaction-picture equation

$$i\hbar \frac{\partial \psi_I(t)}{\partial t} = V_I(t)\psi_I(t) , \tag{5.40}$$

there corresponds the matrix equation

$$i\hbar \frac{\partial \underline{a}(t)}{\partial t} = \underline{V}_I(t)\underline{a}(t) , \tag{5.41}$$

obtained on expanding $\psi_I(t)$ in eigenfunctions of H_0, $\psi_I(t) = \sum a_n(t)\phi_n$. A similar option is exercised here. To the operator equation

$$i\hbar \frac{\partial \ln \rho(t)}{\partial t} = (adH) \ln \rho(t) \tag{5.42}$$

there corresponds the matrix representation

$$i\hbar \frac{\partial \underline{\underline{\lambda}}}{\partial t} = \underline{\alpha}\,\underline{\underline{\lambda}} . \tag{5.43}$$

Similarly, to the operator equation

$$\ln \rho(t) = U \ln \rho(t_0) U^{\dagger} , \tag{5.44}$$

there is the corresponding

$$\underline{\lambda}(t) = \underline{G}\,\underline{\lambda}(t_0) \tag{5.45}$$

matrix equation, etc. An important practical point is that the dimension of the matrix equation, Eqs. (5.43) or (5.45), equals the number of constraints,[62] and that a further reduction in the number of dimensions may be possible.

VI. OVERVIEW

The formalism has two distinct aims. One is to obtain functional forms, containing free parameters, which can be used to analyze experimental (or heavy-computational) results. It was shown that for any given family of similar processes this aspect can be implemented by purely algebraic means. The Hamiltonian is used to generate the dynamic algebra and hence the dynamical group. The $\underline{G}$ matrix is then introduced as the (adjoint) representation of the dynamical group and so is an analytic function of the group parameters. Given an initial state (of maximal entropy, subject to constraints), the $\underline{G}$ matrix specifies the magnitude of the constraints (or of the Lagrange parameters) which determine (via the maximal entropy formalism) the final state. The final state so constructed is an exact solution of the equations of motion. Alternatively, the $\underline{S}$ matrix can be obtained as the (Hilbert space) representation of the dynamical group. The scattering and the density matrices will be (analytic) functions of the group parameters. For any initial state, the number of independent group parameters equals the number of dynamic constraints.

The first aim of the formalism is that of analysis, couched in dynamical theory. The second aim is predictive. Equations of motion (which do have existence theorems for their solutions[56,58]) were derived for the group parameters. When the dynamical algebra is solvable, these equations are demonstrably integrable. It is then possible to explicitly predict, e.g., the dependence of the Lagrange parameters of the final state on the details of the Hamiltonian (say, on the vibrational frequen-

cy) specific to the collision under discussion. It should be clearly noted that the number of coupled differential equations that need be solved is never larger than the dimension of the dynamic algebra (i.e., the number of dynamic constraints). This is so for any initial state, irrespective of the number of constraints required for its specification. Once the group parameters have been solved for, one need use only algebraic procedures to determine the $\underline{G}$ matrix [via Eq. (5.10)] and hence the time evolution of the Lagrange parameters for any set of constraints.

ACKNOWLEDGMENTS

An exceedingly primitive version of the formalism, based on the Fredholm-Schmidt theorem, and a very simple example, were presented in the Ph.D thesis (1964) of one of us (R.D.L.). We would like to thank Professor John T. Lewis for his enthusiasm about that part of the thesis and for strongly urging that it be further developed. This work was supported by the Office of Scientific Research, USAF, under Grant No. AFOSR 77-3135.

APPENDIX A: MATRIX $\underline{G}^0$

The matrix $\underline{G}^0$ is a representation of the dynamical group of H_0, cf. Eq. (4.22). In this appendix we show that if H_0 is time independent and there exists a finite set of operators $\{A_r\}$ that is closed under commutation with H_0 then $\underline{G}^0$ can always be brought to a diagonal form with strictly periodic diagonal matrix elements

$$\overline{G}^0_{rs}(t+\Delta t, t) = \delta_{rs}\, e^{(-i\omega_r \Delta t)} . \tag{A1}$$

The proof is based on the demonstration that under the stated conditions adH_0 can be regarded as a Hermitian (super) operator and hence can be diagonalized with real eigenvalues, i.e., that there exists a set of operators $\{C_r\}$ such that

$$(adH_0)C_r = \hbar\omega_r C_r , \tag{A2}$$

and hence [cf. Eqs. (5.9) and (5.10)]

$$U_0 C_r U_0^\dagger = \exp\{-[i\Delta t(adH_0)]/\hbar\}C_r = \sum_s C_s \overline{G}^0_{sr} = \sum_s e^{(-i\omega_r \Delta t)} C_s \delta_{sr} . \tag{A3}$$

To prove that adH_0 is Hermitian, we need to show that

$$((adH_0)A, B) = (A, (adH_0)B), \tag{A4}$$

where (A,B) is a scalar product, here a scalar product of two operators A and B (since adH_0 acts on operators). As has been discussed before[17,36] one can define such a scalar product by

$$(A,B) = \mathrm{Tr}(\rho A^\dagger B), \tag{A5}$$

where ρ is a positive definite Hermitian "weight" operator. Now

$$\begin{aligned}((adH_0)A, B) - (A, (adH_0)B) &= \mathrm{Tr}\{\rho([H_0,A]^\dagger B - A^\dagger [H_0,B])\} \\ &= \mathrm{Tr}\{[H_0,\rho]A^\dagger B\} .\end{aligned} \tag{A6}$$

Hence (adH_0) is Hermitian if there exists a ρ with the specified properties that commutes with H_0. Since, by assumption, H_0 is time independent such a ρ is provided e.g., by

$$\rho = e^{(-\beta H_0)}/\mathrm{Tr}(e^{(-\beta H_0)}), \tag{A7}$$

and, in general, by an normalizable definite function of H_0, e.g., $\rho = e^{\{f(H_0)\}}$. Q.E.D.

APPENDIX B: ROTATIONAL EXCITATION OF THE SYMMETRIC TOP

This appendix demonstrates the use of group-theoretic techniques to obtain the matrix elements of the evolution operator during (and after) a collision where a symmetric top is perturbed by a dipole potential. We use the group $E(3)$ generated by the six-dimensional Lie algebra introduced in Eq. (3.70). The full text of this appendix is available from the authors upon request.

APPENDIX C: DERIVATIVES OF EXPONENTIAL OPERATORS

Despite a voluminous physics literature on the subject we are not aware of a proof of Eq. (5.15), and so provide one here, following ideas from Ref. 17(b).

For functions of operators that do admit of an inverse and which depend on a parameter, say s

$$\frac{\partial f^{-1}}{\partial s} = -f^{-1}\,\frac{\partial f}{\partial s}\,f^{-1} . \tag{C1}$$

Hence, when a function depends on two parameters, say s and t

$$\frac{\partial(f^{-1}\partial f/\partial t)}{\partial s} - \frac{\partial(f^{-1}\partial f/\partial s)}{\partial t} = \left[f^{-1}\left(\frac{\partial f}{\partial t}\right), f^{-1}\left(\frac{\partial f}{\partial s}\right)\right] . \tag{C2}$$

Let the evolution operator be $U = e^{(A)}$, where $A = A(t)$ and define $f(s,t)$ by $f(s,t) = e^{(-sA)}$. Then

$$f^{-1}\left(\frac{\partial f}{\partial s}\right) = -e^{(sA)}e^{(-sA)}A = -A , \tag{C3}$$

$$W(s,t) = f^{-1}\left(\frac{\partial f}{\partial t}\right) = e^{(sA)}\,\frac{\partial}{\partial t}\,e^{(-sA)} . \tag{C4}$$

The function $W(s,t)$ is defined by Eq. (C4) and what we require is its t dependence for $s = 1$.

Substituting Eqs. (C3) and (C4) in the general relation Eq. (C2)

$$\frac{\partial W}{\partial s} = -\left(\frac{\partial A}{\partial t}\right) + [W, -A] = -\left(\frac{\partial A}{\partial t}\right) + (adA)W . \quad \text{(C5)}$$

In the second line we have used the notation adA introduced in Eq. (3.21). Equation (C5) need be solved subject to the boundary condition $W(s=0,t)=0$. Since the equation is linear one might as well guess the solution

$$W(s,t) = s\phi(sadA)\,\frac{-\partial A}{\partial t} , \quad \text{(C6)}$$

where $\phi(z)$,

$$\phi(z) = \sum_{n=1} \frac{z^{n-1}}{n!} = \int_0^1 e^{(xz)}\,dx = \frac{(e^{(z)}-1)}{z} , \quad \text{(C7)}$$

is a function with a convergent-power-series expansion. The result, Eq. (5.15), in the text is simply Eq. (C6) for $s=1$.

To verify that Eq. (C6) is the solution of Eq. (C5) note that Eq. (C5) is a first-order linear-differential equation and so admits an integrating factor.

Indeed, multiplying both sides of Eq. (C5) by $e^{(-sadA)}$ brings the equation (after some rearrangements) to the form

$$\frac{\partial(e^{(-sadA)}W)}{\partial s} = -e^{(-sadA)}\,\frac{\partial A}{\partial t} . \quad \text{(C8)}$$

Integrating both sides and using the integral representation of $\phi(z)$, Eq. (C7), and the boundary condition $W(s=0,t)=0$ leads to Eq. (C6)

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[33]F. Smithies, *Integral Equations* (Cambridge U. P., Cambridge, 1958).

[34]The only classical complication is that in order to compare with experiment it is necessary to use dynamical variables with quantal counterparts. An explicit example is worked out in Sec. III H.

[35]The matrix G plays a similar role to that of the scattering matrix of the ordinary collision theory. The key difference is that G relates the initial and final values of probabilities rather than of amplitudes (as does the ordinary scattering matrix). Because G determines the evolution of operators [cf. Eq. (2.17)] it can be rightly regarded as the "super" evolution matrix i.e., the evolution matrix in Liouville space (Refs. 23 and 36).

[36]For properties of super operators see Refs. 17, 23 and also, for example; (a) Y. Nambu, Prog. Theor. Phys. 4, 331 (1949); (b) F. J. Murray, J. Math. Phys. 3, 451 (1962); (c) H. Primas, Rev. Mod. Phys. 35, 710 (1963); (d) R. Zwanzig, Physica 30, 1109 (1964); (e) R. A. Marcus, J. Chem. Phys. 53, 1349 (1970).

[37]E. T. Jaynes, *Statistical Physics* (Benjamin, New York, 1963), pp. 181-218.

[38]R. D. Levine, J. Chem. Phys. 65, 3302 (1976).

[39]A coherent state is a limiting form of Eq. (3.10) when $\beta \to \infty$, see, for example, Ref. 22, Eq. (4.10.23). Hence the result that Eq. (3.10) maintains its functional form (with β unchanged) includes the result that a coherent case will remain coherent (Ref. 22) as a special case.

[40]The operator adA is a "superoperator" since it operates on operators. See Refs. 17 and 36.

[41]It will be argued in Sec. V that ρ and U are both elements of a complex Lie group. Hence the group parameters can be regarded as the Lagrange parameters of the dynamic constraints.

[42]W. Miller, Jr., *Lie Theory and Special Functions* (Academic, New York, 1968).

[43]The required operations in going over to the product form consist essentially in repeated application of the identity, Eq. (3.20), to the form, Eq. (3.47). The labor can be reduced considerably by using the group-theoretical machinery developed for this purpose in Sec. V F.

[44](a) R. D. Levine and B. R. Johnson, Chem. Phys. Lett. 8, 501 (1971); (b) R. D. Levine and R. B. Bernstein, J. Chem. Phys. 53, 686 (1970);

[45]See, for example, W. H. Miller, Adv. Chem. Phys. 25, 69 (1974).

[46]L. C. Biedenharn and P. J. Brussaard, *Coulomb Excitation* (Clarendon, Oxford, 1965).

[47]See, for example, (a) K. P. Lawley and J. Ross, J. Chem. Phys. 43, 2930 (1965); (b) R. J. Cross, Jr. and D. R. Herschbach, *ibid.* 43, 3530 (1965); (c) R. B. Bernstein and K. H. Kramer, *ibid.* 44, 4473 (1966); (d) H. A. Rabitz and R. G. Gordon, *ibid.* 53, 1815 (1970).

[48](a) H. A. Rabitz, Annu. Rev. Phys. Chem. 25, 155 (1974); (b) G. G. Balint-Kurti, *Theoretical Chemistry*, edited by D. R. Herschbach (Butterworths, Oxford, 1976).

[49]Note that in order to avoid having factors of $\sqrt{2}$ we have not used the more conventional normalization $\mp (Q_z \pm iQ_y)/\sqrt{2}$.

[50]N. Y. Vilenkin, Trans. Moscow Math. Soc. 4, 209 (1965); N. Y. Vilenkin, E. L. Akim, and A. A. Levin, Dokl. Akad. Nauk. SSSR. 112, 987 (1957).

[51]See, for example, D. M. Brink, and G. R. Satchler, *Angular Momentum* (Clarendon, Oxford, 1968).

[52](a) R. D. Levine, R. B. Bernstein, P. Kahana, I. Procaccia, and E. T. Upchurch, J. Chem. Phys. 64, 796 (1976); (b) I. Procaccia and R. D. Levine, Phys. Rev. A 14, 1569 (1976).

[53]This is a stronger result than that obtained for the density operator (cf. Sec. II G). There, it was necessary that the different initial states will be similarly specified.

[54]S. Lie, *Theorie der Transformationsgruppen* (Engel,

Leipzig, 1888).
[55]Books dealing with parametrizations and representations of Lie groups include (a) W. Miller, Jr., *Lie Theory and Special Functions* (Academic, New York, 1968); (b) N. Y. Vilenkin, *Special Functions and the Theory of Group Representations* (AMS Translations, Providence, 1968); (c) D. Kleima, W. J. Holman, III, and L. C. Biedenharn, in *Group Theory and Its Applications* (Academic, New York, 1968); (d) J. D. Talman, *Special Functions, A Group Theoretical Approach* (Benjamin, New York, 1968).
[56](a) W. Magnus, Comm. Pure Appl. Math. 7, 649 (1954); see also (b) E. H. Wichmann, J. Math. Phys. 2, 876 (1961); (c) P. Pechukas and J. C. Light, J. Chem. Phys. 44, 3897 (1966).
[57]One can use the Zassenhaus formula [H. Zassenhaus, *The Theory of Groups* (Chelsea, New York, 1956)] to transform the canonical representation, Eq. (4.3), to the product form. See, for example, Ref. 36(b) Sec. IV in particular.
[58]J. Wei and E. Norman, Proc. Am. Math. Soc. 15, 327 (1964).
[59]As an illustration consider the elements of the rotation group, traditionally expressed [e.g., A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1962), Eq.(XIII.60)] as $R(\alpha\ \beta\ \gamma) = \exp(-i\alpha J_z)\exp(-i\beta J_y) \times \exp(-i\gamma J_z)$, where the group parameters (i.e., α, β, γ) are the Euler angles.
[60]Of course, the entire discussion is based on the premise that the dynamical algebra is finite. If it is not, then the method of Sec. II has to be used. The Hilbert-Schmidt theorem (Ref. 34) will then play a dominant role.
[61]I. Procaccia, Y. Shimoni, and R. D. Levine, J. Chem. Phys. 65, (1976).
[62]This is the essential feature that distinguishes the present formulation from discussions of quantum mechanics in the "superoperator" or "Liouville space" formulation (Ref. 23).
[63]A. S. Wightman, Rev. Mod. Phys. 34, 845 (1962).
[64]W. Miller, Comm. Pure Appl. Math. 17, 527 (1964).