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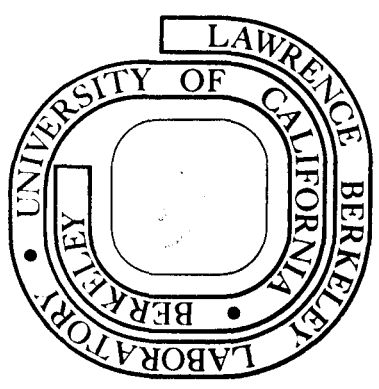
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On the Possibility of Direct Solution of the Classical
Liouville Equation for Inelastic Molecular Collisions;
the Reduced Liouville Equation[†]

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Abstract

Starting with the ordinary classical Liouville equation for the time evolution of phase space distribution functions, total energy conservation is used to obtain a reduced Liouville equation which determines the steady-state (i.e., time-independent) reduced distribution function on the "energy shell" in phase space. Boundary conditions which correspond to time-independent scattering theory are easily imposed, and one sees clearly how to extract the time-independent transition probability matrix for a given total energy; this is the classical analog of the time-independent on-shell S-matrix of quantum scattering theory. The reduced Liouville equation is of a form that is amenable to direct numerical solution, and ways for approaching this are described. A particular approximate version of the reduced Liouville equation is seen to be equivalent to a recently proposed stochastic model.

I. Introduction

Many attributes of inelastic and reactive molecular collision processes are described quite adequately by classical mechanics. Classical trajectory calculations,¹ with Monte Carlo sampling of initial conditions, for example, are in fact a popular and useful tool for studying the dynamics of molecular collision phenomena.

The net result of such trajectory calculations is to map some initial phase space distribution onto a final one, the mapping being accomplished by following individual phase points from the initial asymptotic region before collision to the final asymptotic region after the collision is over. An alternate way of mapping an initial phase space distribution onto a final one is to solve the classical Liouville equation,²

$$i \frac{\partial}{\partial t} \rho(\underline{p}, \underline{q}; t) = L \rho(\underline{p}, \underline{q}; t) \quad , \quad (1.1)$$

where L is the Liouville operator

$$L = i \left[\frac{\partial H(\underline{p}, \underline{q})}{\partial \underline{q}} \cdot \frac{\partial}{\partial \underline{p}} - \frac{\partial H(\underline{p}, \underline{q})}{\partial \underline{p}} \cdot \frac{\partial}{\partial \underline{q}} \right] \quad , \quad (1.2)$$

and $H(\underline{p}, \underline{q})$ is the Hamiltonian function for the system; \underline{p} and \underline{q} are any set of canonically conjugate momenta and coordinates of the system. Eq. (1.1) specifies how the phase space distribution $\rho(\underline{p}, \underline{q}; t)$ evolves in time, and solving it once accomplishes the same thing as computing many individual classical trajectories.

This paper explores the possibility of directly solving the Liouville equation for molecular collision processes. Most earlier work³ along this line has essentially followed Prigogine's^{2,4} analysis: The similarity of

Eq. (1.1) to the time-dependent Schrödinger equation is noted, the equation is Fourier transformed from time space to energy space, the resolvent operator $(z-L)^{-1}$ is introduced (i.e., Greens' functions), a Born-type series used to expand it,

$$(z-L)^{-1} = (z-L_0)^{-1} + (z-L_0)^{-1}L_1(z-L_0)^{-1} + \dots, \quad (1.3)$$

where $L = L_0 + L_1$, etc. Although this approach may be useful for some purposes, it fails to lead to concrete equations that can actually be solved by standard numerical methods. One reason for this is that the phase space distribution function and the various operators involved all contain energy-conserving delta functions that must be formally removed in order to obtain the "on shell" quantities of interest.

In Section II it is shown how the singular structure due to energy conservation can be eliminated at the beginning of the analysis. This leads to a reduced Liouville equation on the "energy shell" in phase space. Solution of this equation for the reduced distribution function leads directly to the physical quantities of interest, i.e., transition probabilities, or cross sections, which correspond to a given total energy. Sections III and IV show how the reduced Liouville equation can be approximated or manipulated to make contact with the results obtained by other approaches, and they also discuss some of the practical aspects of how it can be solved.

At this stage it is not clear that it will be easier in practice to solve the reduced Liouville equation numerically than to compute many individual classical trajectories. The Liouville approach is different,

however, and it does lead to interesting new ways of describing the classical mechanics of molecular collisions. It does seem likely, too, that in some cases it can provide a more useful way for carrying out specific calculations.

II. The Reduced Liouville Equation

To keep the presentation as simple as possible it is useful to consider specifically the simplest inelastic collision system, a non-reactive collinear atom-diatom collision, for which the classical Hamiltonian is

$$H(P,R,p,r) = \frac{P^2}{2\mu} + \frac{p^2}{2m} + v(r) + V(R,r) \quad . \quad (2.1)$$

(P,R) are the momentum and coordinate for the translational degree of freedom, and (p,r) are those for the vibrational degree of freedom; μ and m are the corresponding reduced masses. $v(r)$ is the vibrational potential function of isolated diatomic molecule, and $V(R,r)$ is the intermolecular potential which couples translation and vibration.

It is useful to replace the cartesian variables (p,r) of the diatom by the action-angle variables⁵ (n,q), in terms of which the Hamiltonian is

$$H(P,R,n,q) = \frac{P^2}{2\mu} + \epsilon(n) + V(R,n,q) \quad . \quad (2.2)$$

$\epsilon(n)$ is the energy of the isolated diatom--it is also of the WKB eigenvalue of the oscillator in terms of the action variable n , the classical counterpart of the vibrational quantum number--and

$$V(R,n,q) = V(R,r(n,q)) \quad , \quad (2.3)$$

where $r(n,q)$ is the vibrational coordinate in terms of the action-angle variables. For a harmonic oscillator, for example, one has

$$\varepsilon(n) = \omega n \quad (2.4a)$$

$$r(n, q) = r_0 + \sqrt{\frac{2n}{m\omega}} \cos q \quad (2.4b)$$

where ω is the frequency of the oscillator and r_0 its equilibrium position.

To describe a steady-state scattering situation at a given total energy E , the phase space distribution $\rho(P, R, n, q; t)$ is taken to be time-independent (i.e., steady-state scattering) and proportional to an energy-conserving delta function:

$$\rho(P, R, n, q; t) = \delta[E - H(P, R, n, q)] f(n, q, R) \quad (2.5)$$

The function $f(n, q, R)$ is taken not to be a function of P since the delta function factor determines P in terms of the other variables:

$$P = P_E(R, n, q) \equiv \sqrt{2\mu[E - \varepsilon(n) - V(R, n, q)]} \quad (2.6)$$

(For the moment the fact that two values of P are possible--the + or the - square root--will be ignored.) Substituting this ansatz for ρ , Eq. (2.5), into the Liouville equation, Eq. (1.1), leads in an elementary manner to

$$0 = \delta(E - H) \left[\frac{\partial f}{\partial R} \frac{\partial H}{\partial P} + \frac{\partial f}{\partial q} \frac{\partial H}{\partial n} - \frac{\partial f}{\partial n} \frac{\partial H}{\partial q} \right],$$

and with the Hamiltonian of Eq. (2.2) this becomes

$$0 = \delta[E - H(P, R, n, q)] \left\{ \frac{\partial f}{\partial R} \frac{P}{\mu} + \frac{\partial f}{\partial q} (\varepsilon'(n) + \frac{\partial V}{\partial n}) - \frac{\partial f}{\partial n} \frac{\partial V}{\partial q} \right\} \quad (2.7)$$

The delta function allows P to be set to $P_E(R, n, q)$ in the curly brackets in Eq. (2.7), so that the entire factor in curly brackets is then a function

only of R, n, q (and of course the fixed total energy E). Setting this factor to zero, then gives the reduced Liouville equation on the energy shell,

$$\begin{aligned} \frac{1}{\mu} P_E(R, n, q) \frac{\partial f(n, q, R)}{\partial R} = & - [\epsilon'(n) + \frac{\partial V(R, n, q)}{\partial n}] \frac{\partial f(n, q, R)}{\partial q} \\ & + \frac{\partial V(R, n, q)}{\partial q} \frac{\partial f(n, q, R)}{\partial n} \quad , \end{aligned} \quad (2.8)$$

where $P_E(R, n, q)$ is defined by Eq. (2.6). Since

$$\frac{\partial P_E(R, n, q)}{\partial n} = -\mu [\epsilon'(n) + \frac{\partial V}{\partial n}] / P_E(R, n, q) \quad (2.9a)$$

$$\frac{\partial P_E(R, n, q)}{\partial q} = -\mu \frac{\partial V}{\partial q} / P_E(R, n, q) \quad , \quad (2.9b)$$

the reduced Liouville equation may be written more compactly as

$$\begin{aligned} \frac{\partial f(n, q; R)}{\partial R} = & \frac{\partial P_E(R, n, q)}{\partial n} \frac{\partial f(n, q; R)}{\partial q} \\ & - \frac{\partial P_E(R, n, q)}{\partial q} \frac{\partial f(n, q; R)}{\partial n} \quad . \end{aligned} \quad (2.10)$$

A useful interpretation of the reduced Liouville equation (2.10) is that the translational coordinate R has replaced the time t as the "progress variable" for the collision, and the reduced distribution function $f(n, q; R)$ is the probability distribution in the phase space of the internal degrees of freedom as a function of the progress variable R . (This is the reason for the notation which separates R from the other arguments of f by a semicolon.) One can easily see the form of the reduced Liouville equation

for the case of F degrees of freedom: Eqs. (2.2), (2.6), and (2.10) are modified only in that there are $F-1$ action-angle variables (n_i, q_i) $i = 1, \dots, F-1$; Eq. (2.10) then reads

$$\frac{\partial f(\underline{n}, \underline{q}; R)}{\partial R} = \frac{\partial P_E(R, \underline{n}, \underline{q})}{\partial \underline{n}} \cdot \frac{\partial f(\underline{n}, \underline{q}; R)}{\partial \underline{q}} - \frac{\partial P_E(R, \underline{n}, \underline{q})}{\partial \underline{q}} \cdot \frac{\partial f(\underline{n}, \underline{q}; R)}{\partial \underline{n}} \quad (2.10')$$

where

$$P_E(R, \underline{n}, \underline{q}) = \sqrt{2\mu[E - \epsilon(\underline{n}) - V(R, \underline{n}, \underline{q})]} \quad (2.6')$$

Section IV considers in some detail the modifications in the above formulation that must be made since P is not a single-valued function of $(R, \underline{n}, \underline{q})$, i.e., $P = +P_E$ or $-P_E$. This is related to the fact that R is not a monotonic collision parameter, i.e., during the collision R first decreases and later increases.

For the present this difficulty is side-stepped by making a canonical transformation⁶ which replaces R by a new coordinate that is a monotonic progress variable. Thus the "old" variables $P, R, \underline{n}, \underline{q}$ are replaced by the "new" variables E_0, t_0, N, Q ; it is desired that the new momenta N and E_0 be given in terms of the old variables by

$$N = n$$

$$E_0 = \frac{P^2}{2\mu} + \epsilon(n) + V_0(R) \quad ,$$

where $V_0(R)$ is a reference potential that is chosen to approximate the R -dependence of $V(R, r)$ (e.g., $V_0(R) = V(R, r_0)$, r_0 being the equilibrium value of r). E_0 is thus seen to be an "unperturbed energy", and its

conjugate variable t_0 will be an "unperturbed time". The generating function⁶ which effects this transformation is

$$F_2(q, R; N, E_0) = qN + \int^R dR' \sqrt{2\mu[E_0 - \epsilon(N) - V_0(R')]} \quad , \quad (2.11)$$

and the equations which specify the transformation are⁶

$$n = \frac{\partial F_2}{\partial q} \quad (2.12a)$$

$$P = \frac{\partial F_2}{\partial R} \quad (2.12b)$$

$$Q = \frac{\partial F_2}{\partial N} \quad (2.12c)$$

$$t_0 = \frac{\partial F_2}{\partial E_0} \quad (2.12d)$$

Carrying out the canonical transformation, one finds the Hamiltonian to be given in terms of the new variables by

$$H(E_0, t_0, N, Q) = E_0 + \Delta V(R(t_0, E_0, N), r(N, Q, t_0)) \quad (2.13a)$$

with

$$\Delta V(R, r) \equiv V(R, r) - V_0(R) \quad , \quad (2.13b)$$

where the "old variables" (R, n, q) are given in terms of the new ones (t_0, N, Q) by

$$n = N \quad (2.14a)$$

$$q = Q + \varepsilon'(N)t_0 \quad , \quad (2.14b)$$

and $R(t_0, E_0, N)$ is defined implicitly by the equation

$$t_0 = \int^R dR' \left\{ \frac{2}{\mu} [E_0 - \varepsilon(N) - V_0(R')] \right\}^{-\frac{1}{2}} \quad . \quad (2.14c)$$

It is then not hard to show that the reduced Liouville equation in the new expression, which replaces Eq. (2.10), is

$$\begin{aligned} \frac{\partial f(N, Q; t_0)}{\partial t_0} &= \frac{\partial E_0(t_0, N, Q)}{\partial N} \frac{\partial f(N, Q; t_0)}{\partial Q} \\ &\quad - \frac{\partial E_0(t_0, N, Q)}{\partial Q} \frac{\partial f(N, Q; t_0)}{\partial N} \quad , \end{aligned} \quad (2.15)$$

where $E_0(t_0, N, Q)$ is defined implicitly by energy conservation, $E = E_0 + \Delta V$,
or

$$E_0 = E - \Delta V(R(t_0, E_0, N), r(N, Q, t_0)) \quad . \quad (2.16)$$

$E_0(t_0, N, Q)$ also depends, of course, on the fixed value of the total energy E .

To make the above expressions more concrete it is useful to consider explicitly the example which will be treated in more detail in the following section. The oscillator is taken to be harmonic, so that

$$\varepsilon(N) = \omega N \quad ; \quad (2.17a)$$

the reference potential $V_0(R)$ is an exponential repulsion

$$V_0(R) = e^{-\alpha R} \quad , \quad (2.17b)$$

and $\Delta V(R,r)$ is

$$\Delta V(R,r) = \gamma(r-r_0) V_0(R) \quad . \quad (2.17c)$$

For this case one then has

$$r(N,Q,t_0) - r_0 = \sqrt{\frac{2N}{m\omega}} \cos(Q + \omega t_0) \quad (2.18a)$$

$$R(t_0, E_0, N) = -\frac{1}{2} \ln \left[(E_0 - \omega N) \operatorname{sech}^2 \left(\frac{\alpha t_0}{2} \sqrt{\frac{2}{\mu} (E_0 - \omega N)} \right) \right] \quad , \quad (2.18b)$$

and Eq. (2.16) for $E_0(t_0, N, Q)$ becomes

$$E_0 = E - \gamma [r(N, Q, t_0) - r_0] e^{-\alpha R(t_0, E_0, N)} \quad . \quad (2.18c)$$

Using Eqs. (2.18a) and (2.18b), Eq. (2.18c) for E_0 can be rearranged to the following form

$$E_0 = \frac{E + (\omega N)A}{1 + A} \quad ,$$

where

$$A = \gamma \sqrt{\frac{2N}{m\omega}} \cos(Q + \omega t_0) \operatorname{sech}^2 \left(\frac{\alpha t_0}{2} \sqrt{\frac{2}{\mu} (E_0 - \omega N)} \right) \quad ,$$

which could in practice be solved by successive substitution.

III. The Classical Path Approximation

To get a better physical understanding of the reduced Liouville equation obtained in the previous section and to make contact with some other work, it is useful to consider the "classical path" limit of the equation. It is emphasized, however, that this is in no way a necessary assumption of the present formulation.

a. Basic Equations and Boundary Conditions

In the classical path approximation the translational coordinate R is assumed to be the function of time that is determined by the reference potential $V_0(R)$. The result of this is that the variable t_0 of Eq. (2.15) becomes the actual time, $t_0 \rightarrow t$, and the translational energy $\frac{1}{2} \mu v^2 \equiv E_0 - \omega N$ is constant. In this limit it is easy to show that the reduced Liouville equation, Eqs. (2.15) and (2.16), becomes

$$\begin{aligned} \frac{\partial f(N, Q; t)}{\partial t} = & - \frac{\partial \Delta V(N, Q, t)}{\partial N} \frac{\partial f(N, Q; t)}{\partial Q} \\ & + \frac{\partial \Delta V(N, Q, t)}{\partial Q} \frac{\partial f(N, Q; t)}{\partial N} \quad , \end{aligned} \quad (3.1a)$$

where

$$\Delta V(N, Q, t) \equiv \Delta V(R(t), r(N, Q, t)) \quad (3.1b)$$

Eq. (3.1) is a partial differential equation for f , so to solve it in general requires a basis set expansion in all the variables except t , i.e., in N and Q . For the present we expand only the Q dependence in a basis set. (Section IIIId also expands the N dependence.) Since all quantities are periodic in Q , a Fourier series is the natural choice of

basis set for this variable:

$$f(N, Q; t) = \sum_{k=-\infty}^{\infty} e^{ikQ} C_k(N, t) \quad . \quad (3.2)$$

Proceeding in standard fashion, one substitutes this expansion for f into Eq. (3.1), multiplies by a particular basis function and integrates over Q , thereby obtaining the following set of coupled equations for the Fourier coefficients:

$$i \frac{\partial C_k(N, t)}{\partial t} = \sum_{k'} M_{k, k'}(N, t) C_{k'}(N, t) \quad , \quad (3.3a)$$

where the matrix $M_{k, k'}$ (which is an operator in N space) is defined by

$$M_{k, k'}(N, t) = \frac{1}{2\pi} \int_0^{2\pi} dQ e^{-i(k-k')Q} \left[k' \frac{\partial \Delta V(N, Q, t)}{\partial N} + i \frac{\partial \Delta V(N, Q, t)}{\partial Q} \frac{\partial}{\partial N} \right] \quad . \quad (3.3b)$$

Consider now the boundary conditions for the different equation for $f(N, Q; t)$, and thus for the Fourier coefficients $C_k(N, t)$. Initially, for $t \rightarrow -\infty$, one has some distribution in the initial vibrational action variable N , $P_0(N)$, say. ($P_0(N)$ might, for example, be a delta function, $P_0(N) = \delta(N-N_0)$, corresponding to the definite value N_0 for the initial vibrational action variable.) The conjugate angle variable is random, so that for $t \rightarrow -\infty$ f is independent of Q :

$$f(N, Q; -\infty) = P_0(N) \quad , \quad (3.4a)$$

which implies that the initial condition for the Fourier coefficients is

$$C_k(N, -\infty) = \delta_{k,0} P_0(N) \quad . \quad (3.4b)$$

With this initial condition the first order equations in t , Eq. (3.3), are integrated from $t = -\infty$ to $+\infty$ yielding $f(N, Q; +\infty)$. Only the final distribution in N is physically significant; i.e., the final distribution of the vibrational quantum number, $P(N)$, is obtained by integrating over Q :

$$P(N) = \frac{1}{2\pi} \int_0^{2\pi} dQ f(N, Q; +\infty) \quad , \quad (3.5a)$$

or in terms of the Fourier coefficients it is given by

$$P(N) = C_0(N, +\infty) \quad . \quad (3.5b)$$

Thus only the Fourier coefficient $C_0(N, t)$ is desired, but since it is coupled to all the other coefficients by Eq. (3.3) one cannot in general obtain it without solving simultaneously for all the others.

In concluding this section it is useful to note the explicit form assumed by the reduced Liouville equation and its Fourier expansion for the particular system defined by Eqs. (2.17)-(2.18). In this case the interaction potential is

$$\Delta V(N, Q, t) = \gamma V_0(t) \sqrt{\frac{2N}{m\omega}} \cos(Q + \omega t) \quad , \quad (3.6a)$$

where

$$\begin{aligned}
 V_0(t) &\equiv V_0(R(t)) \\
 &= \frac{1}{2} \mu v^2 \operatorname{sech}^2\left(\frac{\alpha v t}{2}\right) .
 \end{aligned} \tag{3.6b}$$

The reduced Liouville equation, Eq. (3.1), then reads

$$\begin{aligned}
 \frac{\partial f(N, Q; t)}{\partial t} &= -\gamma V_0(t) \left[\frac{\cos(Q+\omega t)}{\sqrt{2Nm\omega}} \frac{\partial f(N, Q; t)}{\partial Q} \right. \\
 &\quad \left. + \sqrt{\frac{2N}{m\omega}} \sin(Q+\omega t) \frac{\partial f(N, Q; t)}{\partial N} \right] ,
 \end{aligned} \tag{3.7}$$

and Eq. (3.3) for the Fourier coefficients is found to be

$$\begin{aligned}
 i \frac{\partial C_k(N, t)}{\partial t} &= \frac{1}{2} \gamma V_0(t) \left[\frac{k-1}{\sqrt{2Nm\omega}} e^{i\omega t} C_{k-1}(N, t) + \frac{k+1}{\sqrt{2Nm\omega}} e^{-i\omega t} C_{k+1}(N, t) \right. \\
 &\quad \left. - \sqrt{\frac{2N}{m\omega}} e^{i\omega t} \frac{\partial C_{k-1}(N, t)}{\partial N} + \sqrt{\frac{2N}{m\omega}} e^{-i\omega t} \frac{\partial C_{k+1}(N, t)}{\partial N} \right] .
 \end{aligned} \tag{3.8}$$

b. Relation to a Stochastic Model

It is interesting to note that the stochastic model recently discussed by Schatz, McLafferty, and Ross⁷ corresponds to the coupled equations Eq. (3.8) with only the terms $k = 0, \pm 1$ retained in the Fourier expansion. Keeping only the lowest order harmonics in the Q dependence of $f(N, Q; t)$ is thus the stochastic approximation as viewed in the present formulation. It is analogous to keeping only the "slow" variables, or modes, in mode-mode coupling theory of statistical mechanics.

To see this, consider Eq. (3.8) specifically for the cases $k = 0, \pm 1$:

$$i \frac{\partial C_0(N,t)}{\partial t} = \frac{1}{2} \gamma V_0(t) \left[-\frac{e^{i\omega t}}{\sqrt{2Nm\omega}} C_{-1}(N,t) + \frac{e^{i\omega t}}{\sqrt{2Nm\omega}} C_{+1}(N,t) - \sqrt{\frac{2N}{m\omega}} e^{i\omega t} \frac{\partial C_{-1}(N,t)}{\partial N} + \sqrt{\frac{2N}{m\omega}} e^{-i\omega t} \frac{\partial C_{+1}(N,t)}{\partial N} \right] \quad (3.9a)$$

$$i \frac{\partial C_{\pm 1}(N,t)}{\partial t} = \mp \frac{1}{2} \gamma \dot{V}_0(t) \sqrt{\frac{2N}{m\omega}} e^{\pm i\omega t} \frac{\partial C_0(N,t)}{\partial N}, \quad (3.9b)$$

where the terms involving $C_{\pm 2}(N,t)$ have been discarded in Eq. (3.9b).

Eq. (3.9b) is then solved for $C_{\pm 1}$ in terms of C_0 ,

$$C_{\pm 1}(N,t) = \pm i \frac{\gamma}{2} \sqrt{\frac{2N}{m\omega}} \int_{-\infty}^t dt' V_0(t') e^{\pm i\omega t'} \frac{\partial C_0(N,t')}{\partial N}, \quad (3.10)$$

where the boundary condition $C_{\pm 1}(N, -\infty) = 0$ has been used. Substituting $C_{\pm 1}$ from Eq. (3.10) into Eq. (3.9a) then gives (after some arithmetic) the following integro-differential equation for C_0 :

$$\frac{\partial C_0(N,t)}{\partial t} = \frac{\gamma^2 V_0(t)}{m\omega} \int_{-\infty}^t dt' V_0(t') \cos[\omega(t'-t)] \left[\frac{\partial C_0(N,t')}{\partial N} + N \frac{\partial^2 C_0(N,t')}{\partial N^2} \right], \quad (3.11)$$

which is the equation obtained by Schatz et al.⁷ using the Zwanzig-Mori formalism.

c. A Formally Exact Equation for $C_0(N,t)$

In the spirit of the preceding section it is possible to obtain an exact equation for $C_0(N,t)$ by formally solving for all the Fourier coefficients $\{C_k\}$, $k \neq 0$, in terms of C_0 and thus eliminating them from the equations. This is desirable, of course, since it only the one coefficient C_0 that is ultimately needed (cf. Eq. (3.5b)).

This is accomplished by a projection operator decomposition analogous to the Feshbach⁸ P-Q procedure. Eq. (3.3) is written in "partitioned" form, separating the $k = 0$ component from all others:

$$i \frac{\partial C_0(N,t)}{\partial t} = M_{0,0}(N,t) C_0(N,t) + \sum_{k'}' M_{0,k'}(N,t) C_{k'}(N,t) \quad (3.12a)$$

$$i \frac{\partial C_k(N,t)}{\partial t} = M_{k,0} C_0(N,t) + \sum_{k'}' M_{k,k'}(N,t) C_{k'}(N,t) \quad , \quad (3.12b)$$

$$k \neq 0 \quad ,$$

where the prime on the summation means that the $k' = 0$ term is omitted.

Eq. (3.12b) can be formally solved for $\{C_k(N,t)\}$, $k \neq 0$, in terms of $C_0(N,t)$. Taking into account the initial condition $C_k(N,-\infty) = 0$ for $k \neq 0$, this formal solution is

$$C_k(N,t) = \sum_{k'}' \int_{-\infty}^t dt' \{T \exp[-i \int_{t'}^t dt'' \tilde{M}(t'')]\}_{k,k'} M_{k',0}(t') C_0(N,t') \quad ,$$

$$k \neq 0 \quad , \quad (3.13)$$

where T is the usual chronological ordering operator⁹ affecting the exponential operator. The notation $\tilde{M}(t)$ indicates that the $k = 0$ row and column of the matrix $M(t)$ are deleted in constructing the exponential matrix. (In practice this time ordering exponential operator would be evaluated by dividing the time integral into increments and multiplying the exponential matrices for short time intervals.)¹⁰ Substituting Eq. (3.13) into Eq. (3.12a) gives the closed equation for $C_0(N,t)$,

$$i \frac{\partial C_0(N,t)}{\partial t} = M_{0,0}(t) C_0(N,t) + \int_{-\infty}^t dt' K(t,t') C_0(N,t') \quad , \quad (3.14a)$$

where the "memory kernel" $K(t, t')$ is

$$K(t, t') = \sum_{k, k'} M_{0, k}(t) \left\{ T \exp \left[-i \int_{t'}^t dt'' \tilde{M}(t'') \right] \right\}_{k, k'} M_{k', 0}(t'). \quad (3.14b)$$

It should be remembered, too, that $K(t, t')$ is an operator in N -space.

Eq. (3.14) is probably not useful for direct calculations since constructing the memory kernel may be as difficult as solving the original set of equations Eq. (3.3). It may be useful, however, to investigate the qualitative behavior of the memory kernel $K(t, t')$ to learn what phenomenological models might be appropriate in various limiting situations; e.g., does it have a particular simple form if the collision proceeds via a long-lived collision complex? The stochastic model, Eq. (3.11), could be obtained directly from Eq. (3.14) by keeping only the $k, k' = \pm 1$ terms in the matrix products.

d. Basis Set Expansion

To solve Eq. (3.3) by direct numerical methods it is necessary also to expand the N dependence of the reduced distribution function in a basis set:

$$f(N, Q; t) = \sum_{k, \ell} e^{ikQ} \phi_{\ell}(N) c_{k\ell}(t), \quad (3.15)$$

where $\{\phi_{\ell}(N)\}$ is some complete set of functions (taken to be orthonormal) for the interval $0 \leq N < \infty$. (For example, ϕ_{ℓ} might be an exponential function times Laguerre polynomials.) Substituting the expansion Eq. (3.15) into the reduced Liouville equation Eq. (3.1), multiplying

by a particular basis function $e^{ikQ} \phi_\ell(N)$, and integrating over Q and N gives the following set of coupled equations for the expansion coefficients:

$$i \frac{dC_{k\ell}(t)}{dt} = \sum_{k', \ell'} M_{k\ell, k'\ell'}(t) C_{k'\ell'}(t) \quad , \quad (3.16a)$$

where the matrix $M_{k\ell, k'\ell'}(t)$ is given by

$$M_{k\ell, k'\ell'}(t) = \frac{1}{2\pi} \int_0^{2\pi} dQ \int_0^\infty dN e^{-i(k-k')Q} \phi_\ell(N)^* \left[k' \frac{\partial \Delta V(N, Q, t)}{\partial N} \phi_{\ell'}(N) + i \frac{\partial \Delta V(N, Q, t)}{\partial Q} \frac{\partial \phi_{\ell'}(N)}{\partial N} \right] \quad . \quad (3.16b)$$

It is not difficult to show that the matrix \underline{M} is hermitian, so that Eq. (3.16) is of the same form as a matrix representation of the time-dependent Schrödinger equation.¹⁰ The initial condition for the coefficients $C_{k\ell}(t)$ is

$$C_{k\ell}(-\infty) = \delta_{k,0} \int_0^\infty dN \phi_\ell(N)^* P_0(N) \quad , \quad (3.17)$$

where $P_0(N)$ is again the initial distribution for the vibrational quantum number N . The formal solution to Eq. (3.16) is¹⁰

$$C_{k\ell}(t) = \sum_{k', \ell'} \{ T \exp[-i \int_{-\infty}^t dt' \underline{M}(t')] \}_{k\ell, k'\ell'} C_{k'\ell'}(-\infty) \quad , \quad (3.18)$$

where T is again the chronological ordering operator. Because of the initial conditions, Eq. (3.17), only the $k' = 0$ term contributes to the sum in Eq. (3.18), and as discussed in Section IIIa, only the $k = 0$

component of the distribution function is desired as $t \rightarrow +\infty$. For $k = 0$ and $t \rightarrow +\infty$ Eq. (3.18) thus reads

$$C_{0\ell}^{(+\infty)} = \sum_{\ell'} P_{\ell, \ell'} C_{0\ell'}^{(-\infty)}, \quad (3.19)$$

where

$$P_{\ell, \ell'} = \{T \exp[-i \int_{-\infty}^{\infty} dt \underline{M}(t)]\}_{0\ell, 0\ell'} \quad (3.20)$$

By virtue of Eq. (3.19) one recognizes the matrix $P_{\ell, \ell'}$ of Eq. (3.20) as the " ℓ -representation" of the vibrational transition probability. It is the direct analog of the S-matrix in quantum scattering theory. It is the matrix which maps the ℓ -representation of the initial vibrational state distribution, $C_{0\ell}^{(-\infty)}$, onto the ℓ -representation of the final vibrational state distribution, $C_{0\ell}^{(+\infty)}$. Using the completeness of the ℓ -basis set $\{\phi_{\ell}(N)\}$ it is easy to construct P in other representations; e.g., in the N -representation it is

$$P(N, N_0) = \sum_{\ell, \ell'} \phi_{\ell}(N) P_{\ell, \ell'} \phi_{\ell'}(N_0)^* \quad (3.21)$$

The physical meaning of $P(N, N_0)$ is that it is the distribution of the action variable N that results from a collision for which N_0 is the initial value of the action. It is the kernel from which any initial distribution $P_0(N_0)$ is mapped onto the corresponding final distribution $P(N)$:

$$P(N) = \int_0^{\infty} dN_0 P(N, N_0) P_0(N_0) \quad (3.22)$$

It is natural to call $C_{0\ell}(-\infty)$ the ℓ^{th} moment of the initial distribution of the vibrational action variable, and $C_{0\ell}(+\infty)$ is the ℓ^{th} moment of the final distribution. Thus the matrix $P_{\ell,\ell}$ is the "moment representation" of the vibrational transition probability. The inverse of Eq. (3.22) expresses it in terms of $P(N,N_0)$:

$$P_{\ell,\ell} = \int_0^\infty dN \int_0^\infty dN_0 \phi_\ell(N)^* P(N,N_0) \phi_\ell(N_0) \quad (3.23)$$

The practical evaluation of $P_{\ell,\ell}$ from Eq. (3.20) would be easiest by making successive use of the first order Magnus approximation.¹⁰ Thus the total collision time is divided into intervals by the values $t_1 < t_2 < \dots < t_K$, with $t_1 \rightarrow -\infty$, $t_K \rightarrow +\infty$, and in each time interval the first order Magnus approximation is used, giving

$$P_{\ell,\ell} = \left\{ \exp\left[-i \int_{t_1}^{t_2} dt \underline{\underline{M}}(t)\right] \cdot \exp\left[-i \int_{t_2}^{t_3} dt \underline{\underline{M}}(t)\right] \cdot \dots \exp\left[-i \int_{t_{K-1}}^{t_K} dt \underline{\underline{M}}(t)\right] \right\}_{0\ell,0\ell} \quad (3.24)$$

where the matrix $\underline{\underline{M}}(t)$ is defined by Eq. (3.16b).

Within the classical path approximation Eq. (3.24) is the final working expression from which a direct numerical calculation would begin. $P_{\ell,\ell}$, the ℓ -representation of the transition probability matrix, is the complete solution of the classical scattering problem.

IV. Further Discussion of the Reduced Liouville Equation

The discussion of the classical-path limit of the reduced Liouville equation in Section III has shown a number of its salient features and a way one might solve it in practice (i.e., by basis set expansion). In general, however, one does not wish to make the classical path approximation, so we now return to a discussion of the exact reduced Liouville equation obtained in Section II.

The discussion pertaining to Eq. (2.15) showed one way of dealing with the fact that the translational coordinate R is not a monotonic collision variable, or equivalently, that the translational momentum P is not a single-valued function of R, n, q and E . For many purposes this approach might be adequate; this would be particularly true if the potential function $\Delta V(R, r)$ were of an algebraic form that allowed one to solve Eq. (2.16) and obtain $E_0(t_0, N, Q)$ explicitly. All of the techniques discussed in Section III--for example, the basis set expansion discussed in Section III d--carry over in a rather obvious manner to the exact reduced Liouville equation, Eq. (2.15).

This section, however, explores the nature of the Liouville equation where the translational coordinate R is retained as the progress variable. This might be desirable, for example, when it is not possible to solve Eq. (2.16) explicitly for $E_0(t_0, N, Q)$. Returning to the discussion preceding Eq. (2.5), consider the following slightly modified ansatz for the distribution function ρ :

$$\rho(P, R, n, q; t) = \delta[E - H(P, R, n, q)] F(P, R, n, q) \quad ; \quad (4.1)$$

here the coefficient of the delta function is considered to be a function of P also. The energy conserving delta function requires that P be either

$$P = + P_E(R, n, q)$$

or

$$- P_E(R, n, q) \quad , \quad (4.2)$$

where

$$P_E(R, n, q) \equiv \sqrt{2\mu[E - \epsilon(n) - V(R, n, q)]} \geq 0 \quad . \quad (4.3)$$

To separate the two possibilities, note that

$$\begin{aligned} \delta[E - \epsilon(N) - V(R, n, q) - \frac{P^2}{2\mu}] &= \delta\left[\frac{P_E(R, n, q)^2}{2\mu} - \frac{P^2}{2\mu}\right] \\ &= \frac{\mu}{P_E} [\delta(P - P_E) + \delta(P + P_E)] \quad . \end{aligned} \quad (4.4)$$

Defining $f_{\pm}(n, q, R)$ by

$$f_{\pm}(n, q, R) \equiv F(\pm P_E(R, n, q), R, n, q) \quad , \quad (4.5)$$

the new ansatz of Eq. (4.1) becomes

$$\begin{aligned} \rho(P, R, n, q; t) &= \delta[P - P_E(R, n, q)] f_{+}(n, q, R) \mu / P_E(R, n, q) \\ &+ \delta[P + P_E(R, n, q)] f_{-}(n, q, R) \mu / P_E(R, n, q) \quad . \end{aligned} \quad (4.6)$$

Substituting this revised ansatz for ρ , Eq. (4.6) into the Liouville equation, Eq. (1.1), and using standard rules for differentiating and manipulating delta functions, leads to

$$0 = \delta[P - P_E(R, n, q)] \left\{ -\frac{\partial f_+}{\partial R} + \frac{\partial P_E}{\partial n} \frac{\partial f_+}{\partial q} - \frac{\partial P_E}{\partial q} \frac{\partial f_+}{\partial n} \right\} \\ + \delta[P + P_E(R, n, q)] \left\{ \frac{\partial f_-}{\partial R} + \frac{\partial P_E}{\partial n} \frac{\partial f_-}{\partial q} - \frac{\partial P_E}{\partial q} \frac{\partial f_-}{\partial n} \right\}, \quad (4.7)$$

which for $P_E(R, n, q) \neq 0$ is equivalent to the two equations

$$\frac{\partial f_{\pm}(n, q; R)}{\partial R} = \pm \left[\frac{\partial P_E(R, n, q)}{\partial n} \frac{\partial f_{\pm}(n, q; R)}{\partial q} - \frac{\partial P_E(R, n, q)}{\partial q} \frac{\partial f_{\pm}(n, q; R)}{\partial n} \right]. \quad (4.8)$$

In light of their definition in Eq. (4.5), one sees that f_+ and f_- must be the same on the surface defined by $P_E(R, n, q) = 0$; i.e.,

$$f_+(n, q; R) = f_-(n, q; R) \quad (4.9a)$$

for

$$R = R_0(n, q), \quad (4.9b)$$

where $R_0(n, q)$ is the root of the equation $P_E(R_0, n, q) = 0$, or

$$E = \varepsilon(n) + V(R_0, r(n, q)) \quad (4.10)$$

Eq. (4.8) gives the equations of motion for the two functions $f_+(n, q; R)$ and $f_-(n, q; R)$, and Eq. (4.9) states that f_+ and f_- are identical on the "turning point surface" $R = R_0(n, q)$. It is thus clear how the scattering boundary conditions are introduced: For large R the initial distribution

determines $f_-(n, q; R)$, the incoming distribution,

$$f_-(n, q; +\infty) = P_0(n) \quad , \quad (4.11)$$

where as before $P_0(n)$ is the initial distribution in the vibrational action variable n . Eq. (4.8) for $f_-(R, n, q)$,

$$\frac{\partial f_-(n, q; R)}{\partial R} = - \frac{\partial P_E(R, n, q)}{\partial n} \frac{\partial f_-(n, q; R)}{\partial q} + \frac{\partial P_E(R, n, q)}{\partial q} \frac{\partial f_-(n, q; R)}{\partial n} \quad , \quad (4.12a)$$

is then integrated inward in R to determine the value of f_- on the turning point surface $R_0(n, q)$. Eq. (4.9) requires that this also be the value of f_+ on the turning point surface. With f_+ thus determined on the turning point surface, one now integrates Eq. (4.8) for f_+ outward in R ,

$$\frac{\partial f_+(n, q; R)}{\partial R} = \frac{\partial P_E(R, n, q)}{\partial n} \frac{\partial f_+(n, q; R)}{\partial q} - \frac{\partial P_E(R, n, q)}{\partial q} \frac{\partial f_+(n, q; R)}{\partial n} \quad , \quad (4.12b)$$

and from the asymptotic value of f_+ one obtains the final probability distribution of the action variable:

$$P(n) = \frac{1}{2\pi} \int_0^{2\pi} dq f_+(n, q; +\infty) \quad . \quad (4.13)$$

In practice, Eq. (4.12) will in general be solved by a basis set expansion similar to that described in Section IIIId. Thus, $f_+(R)$ and f_- are expanded as

$$f_{\pm}(n, q; R) = \sum_{k, \ell} e^{ikq} \phi_{\ell}(n) C_{k\ell}^{\pm}(R) \quad , \quad (4.14)$$

and the coupled equations for $\{C_{k\ell}^+(R)\}$ and $\{C_{k\ell}^-(R)\}$ are

$$i \frac{dC_{k\ell}^{\pm}(R)}{dR} = \pm \sum_{k', \ell'} M_{k\ell, k'\ell'}(R) C_{k'\ell'}^{\pm}(R), \quad (4.15)$$

where

$$M_{k\ell, k'\ell'}(R) = \frac{1}{2\pi} \int_0^{2\pi} dq \int_0^{\infty} dn e^{-i(k-k')q} \phi_{\ell}(n)^* \left[-k' \frac{\partial P_E(R, n, q)}{\partial n} \phi_{\ell'}(n) - i \frac{\partial P_E(R, n, q)}{\partial q} \frac{\partial \phi_{\ell'}(n)}{\partial n} \right]. \quad (4.16)$$

The boundary condition $f_+ = f_-$ on the turning point surface can be implemented in the following simplified way: Eq. (4.15) for $\zeta^+(R)$ and $\zeta^-(R)$ differ only in the sign of the square root function in Eq. (4.16). Thus $\zeta^+(R)$ and $\zeta^-(R)$ are the analytic continuation of each other; i.e., if one traces the value of $\zeta^-(R)$ around a curve in the complex R-plane which includes the zero of the square root, $\zeta^-(R)$ will change into $\zeta^+(R)$. One thus integrates the following single set of equations

$$i \frac{d\zeta(R)}{dR} = -M(R) \cdot \zeta(R) \quad (4.17)$$

along the contour in the R-plane indicated in Figure 1. $\zeta(R)$ is essentially $\zeta^-(R)$ on an upper part of the contour, and as the contour circles around the turning point region, it changes smoothly into $\zeta^+(R)$; Eq. (4.17) also changes smoothly into the equation for $\zeta^+(R)$ because the square root--and thus P_E --changes sign. The boundary conditions for the integration are therefore

$$\lim_{\substack{R \rightarrow +\infty \\ \text{Im}R > 0}} C_{k\ell}(R) = \delta_{k,0} \delta_{\ell,\ell_0} \quad , \quad (4.18a)$$

and after integrating Eq. (4.17) along the contour in Figure 1, the transition probability is given in the ℓ -representation by

$$P_{\ell,\ell_0} = \lim_{\substack{R \rightarrow \infty \\ \text{Im}R < 0}} C_{0\ell}(R) \quad . \quad (4.18b)$$

It should be noted that the above procedure will be possible only if the potential function $V(R,r)$ is monotonically repulsive in the R coordinate so that there is only one solution of Eq. (4.10) for the turning point $R_0(r(n,q))$. If Eq. (4.10) has more than one solution, as would be the case if $V(R,r)$ had an attractive well in the R coordinate, then for some values of n and q there will be more than one turning point. The boundary conditions are still that $f_+ = f_-$ on the turning point surfaces, but the matching procedure would be more complicated.

V. Concluding Remarks

This paper has derived a reduced Liouville equation which describes the evolution of phase space distributions on the energy shell. The equation has no remaining singular structure due to energy conservation and is amenable to solution by standard methods. The transition probability matrix (on the energy shell) is obtained directly from the asymptotic boundary conditions of the reduced distribution function.

Apart from providing a different kind of insight into the classical mechanics of molecular collisions, there are two situations for which this Liouville approach might be a desirable way to carry out specific calculations. First, solution of the coupled equations, Eq. (3.3) or Eq. (4.17), leads directly to the transition probability in the moment representation, P_{ℓ, ℓ_0} (cf. Eqs. (3.20) or (4.18)), and sometimes this may be the specific quantity of interest rather than the distribution $P(N, N_0)$ in the N-representation itself. There is reason to believe, too, that the lowest order elements of the moment matrix P_{ℓ, ℓ_0} may be much more rapidly convergent with basis set size than are the higher moments which are necessary if the full distribution in the N-representation is to be constructed. Schatz et al.,⁷ for example, found that their approximate equation, which corresponds to keeping only the $k = 0, \pm 1$ terms in the Fourier expansion of the Q-dependence of the distribution function, gave good results for the first and second moments of the distribution but not for the higher ones.

Second, it may be that the Liouville approach will be practically important for collisions that can form long-lived collision complexes. It is well known that it becomes very difficult to follow individual

classical trajectories in this case,¹¹ so that the ability to handle this kind of collision mechanics would be a useful contribution. It should be noted that complex formation cannot take place within the classical path approximation, so that the approach outlined in Section IV is essential. As noted at the end of Section IV, however, the boundary conditions for the reduced Liouville equation are more complicated if $V(R,r)$ have a well in the R -variable--which is necessary for the existence of a collision complex--but it still appears that this can be an important case for the application of the reduced Liouville equation.

It would also be interesting to investigate the extent to which semiclassical extensions of classical mechanics can be incorporated within the Liouville approach. The simplest thing that can be done is to use the Wigner distribution function¹² corresponding to a given initial and final vibrational state. The Wigner distribution function in the cartesian coordinate and momentum (p,x) for a harmonic oscillator in vibrational state ℓ is¹³,

$$\Gamma_{\ell}(p,x) = 2e^{-2n(p,x)} L_{\ell}^{(0)}(4n(p,x)) \quad , \quad (5.1)$$

where $n(p,x) = [\frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2]/\hbar\omega$ and $L_{\ell}^{(0)}$ is a Laguerre polynomial.

Replacing (p,x) by the action-angle variables (n,q) , one sees that if the basis set $\{\phi_{\ell}(n)\}$ of Sections III and IV is chosen as

$$\phi_{\ell}(n) = 2e^{-2n} L_{\ell}^{(0)}(4n) \quad , \quad (5.2)$$

then the ℓ -representation of the transition probability, P_{ℓ,ℓ_0} , can be

interpreted as the transition probability from the initial vibrational state ℓ_0 to the final vibrational state ℓ . This semiclassical feature can thus be easily incorporated in the present approach, but one knows that it does not include all semiclassical effects.¹³

Finally, more work needs to be done in order to describe reactive processes within the present formalism. Here there exist at least two different asymptotic regions, and the boundary conditions for the reduced Liouville equation will be more complicated. This is an important direction for future work.

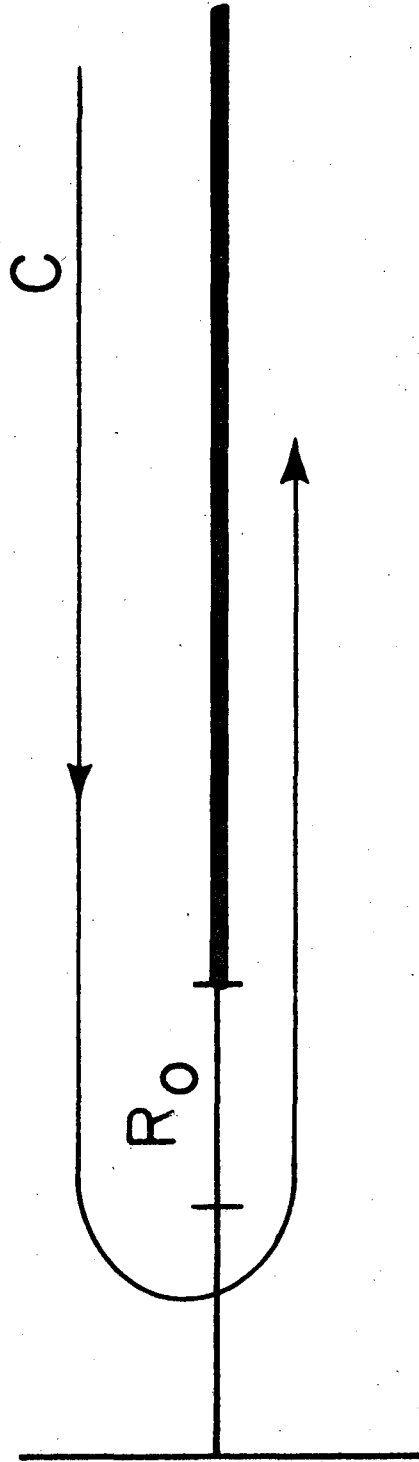
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Figure Caption. Curve C is the contour in the complex R-plane along which Eq. (4.17) is integrated. The heavy black line is the branch cut for the square root function, and the interval labeled R_0 indicates the range of values of the turning point function $R_0(n, q)$ for various values of n and q.

R-plane



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Fig. 1

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