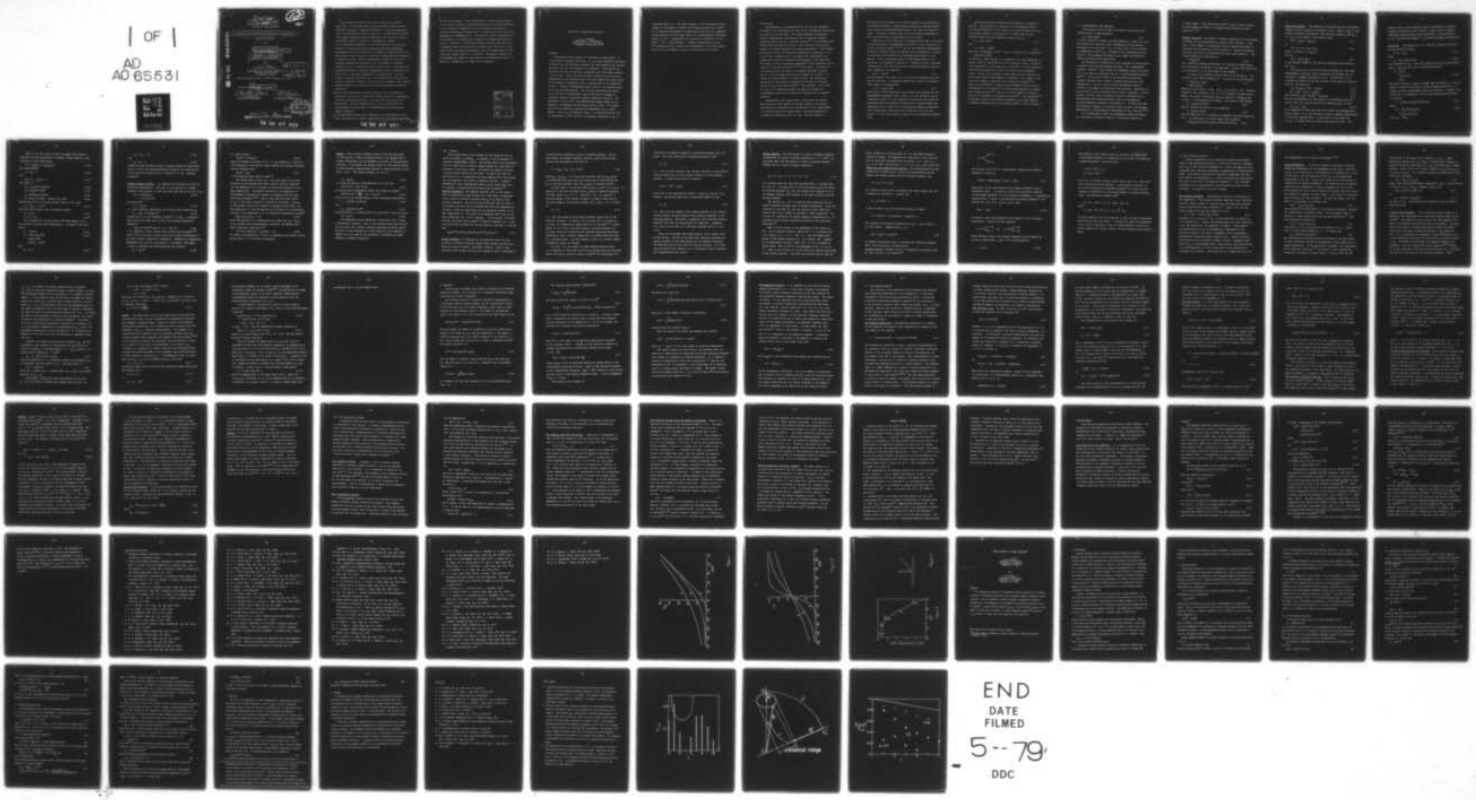
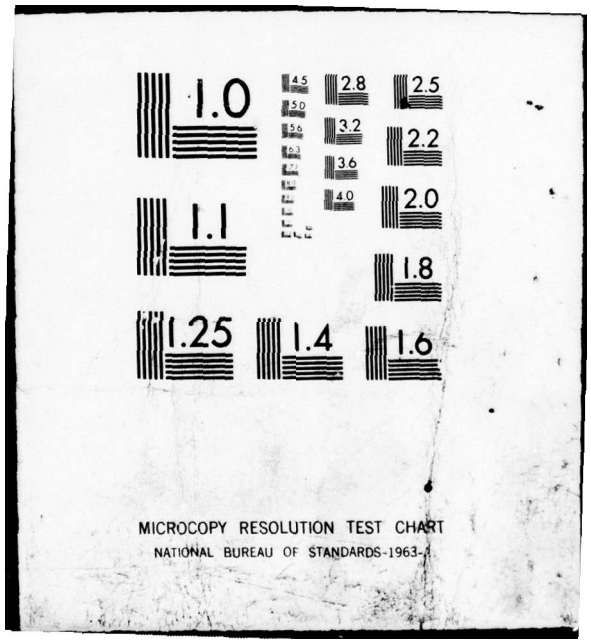
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# (6) STRUCTURAL AND DYNAMIC CONSIDERATIONS IN MOLECULAR COLLISION THEORY.

by

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Work under this Contract has been initiated in several directions. In one major and one minor projects there has been sufficient progress to warrant publication. These are discussed below and detailed accounts are enclosed. Two additional projects which appear promising require additional work and are only mentioned here (under (c) below) as a preliminary account.

(a) A theoretical framework for the interpretation of structural effects in reactive molecular collisions has been formulated. The approach has been presented in a number of seminars and at the NBS meeting 'Current Status of Kinetics of Elementary Gas Reactions ' A detailed account, entitled 'Reactivity, Energy and Structure', has been prepared for publication (in the Journal of Physical Chemistry), and is enclosed as part of this report. The formalism developed therein is primarily thermodynamic-like in character and hence fails to provide a mechanistic interpretation. A first attempt to provide one (section 7) was restricted to reactions on a given electronic surface. Future work will examine a more refined approach aimed at an extension to processes including electronic excitation.

(b) An exact information theoretic solution to the problem of a collinear collision of an atom with a Morse type (i.e. anharmonic) oscillator has been provided. An account has been prepared for publication. The work demonstrates a novel technique for the determination of constraints in problems which at first glance appear insoluble.

(c) Preliminary work has been carried out on the question of the exact definition of a 'prior' expectation for the overall magnitude

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of the rate constant. Such a definition is particularly relevant to electronic excitation processes because of the large differences in the available energy that can occur between the different reaction products. It appears that a natural definition free from ambiguity is indeed feasible. The basis for these developments is the appendix to the manuscript 'Reactivity, Energy and Structure' which is enclosed. A related development has been the search for a formalism that will explicitly recognise that often one is only able to make some general statements about the Hamiltonian of the system but cannot specify it in detail. Preliminary results are encouraging and numerical experiments (in collaboration with W. S. Warren, S. Mukamel and A. Pines) are in progress.

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# Reactivity, Energy and Structure

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Abstract

The reaction rate constant is expressed as $Z\exp(-G_a/RT)$. Z is the binary collision frequency. $G_a$, the free energy of activation, is shown to be the difference between the free energy of the reactive reactants and the free energy of all reactants. The results are derived from both a statistical mechanical and a collision theoretic point of view. While the later is more suitable for an ab-initio computation of the reaction rate, it is the former that lends itself to the search of systematics and of correlations and to compaction of data. Different thermodynamic-like routes to the chatacterisation of $G_a$ are thus explored. The two most promising ones appear to be the use of thermodynamic type cycles and the changes of dependent variables using the Legendre transform technique. The dependence of $G_a$ on $\Delta G^o$, the standard free energy change in the reaction, is examined from the later point of view. It is shown that one can rigorously express this dependence as $G_a = \alpha\Delta G^o + G_a^o M(\alpha)$. Here $\alpha$ is the Brønsted slope, $\alpha = -\partial \ln k(T)/\partial(\Delta G^o/RT)$, $G_a^o$ is independent of $\Delta G^o$ and $M(\alpha)$, the Legendre transform of $G_a$, is

a function only of $\alpha$. For small changes in $\Delta G^{\circ}$, the general result reduces to the familiar 'linear' free energy relation $\delta G_a = \alpha \delta \Delta G^{\circ}$. It is concluded from general considerations that $M(\alpha)$ is a symmetric, convex function of $\alpha$ and hence that $\alpha$ is a monotonically increasing function of $\Delta G^{\circ}$. Experimental data appear to conform well to the form $\alpha = 1/[1 + \exp(-\Delta G^{\circ}/G_a^{\circ})]$. A simple interpretation of the $\Delta G^{\circ}$ dependence of $G_a$, based on an interpolation of the free energy from that of the reagents to that of the products is offered.

## Introduction

Thermodynamics is distinguished not only by the systematic statement of its principles but also by the considerable compactness and order in its data base. This paper explores the question whether thermodynamic-like methods can be formulated towards achieving similar goals in chemical kinetics.[2,3] Such methods have already been explored for relative rate constants, with special emphasis on energy disposal and energy requirements.[4] Here however we are particularly concerned with examining the magnitude of the overall rate constant and its variation both with energy (e.g. temperature) and with structural modifications of the reactants. The search for such systematics preceeded[5-8] even transition state theory[3,9], and has continued[2,3,10-28] ever since. The point of view adopted here will however be somewhat different and will follow a line of reasoning started by Tolman[5] and La Mer[6]. To reduce the formal results to concrete terms, the operational definition of the Brønsted[7] exponent and the idea of chemical inertia due to Evans and Polanyi[10,11] are employed. In a different vein, it is explored whether the familiar concept of a thermodynamic cycle can be adapted for applications in chemical kinetics.

Specifically, this paper offers a derivation and simple applications of the concept of the free energy of activation. The derivation is based on the introduction of the 'distribution of reactive reactants'[5] using either a collision-theoretic or a statistical mechanics point of view. The free energy of

activation is then shown to be the free energy of the distribution of reactive reactants. Applications include both rigorous results (e.g. cycles) and approximations based on the idea of a Brønsted slope. The type of kinetic data that can be used to advantage to test the theory and to guide future work is noted.

Reactivity, or the fraction of collisions that lead to reaction, is discussed from a thermodynamic-like point of view in section II. It was previously argued[4,29-31] that one can introduce thermodynamic functions and hence cycles for systems not in equilibrium. Section III explores the possibility of comparing reactivities in this fashion. Other theoretical routes to the determination of the reactivity are examined in section IV. Finally, section V provides a discussion of the reactivity from a collision-theoretic point of view, leading to the expression

$$k_r(T) = Zp_r(T) \qquad (1.1)$$

for the reaction rate where Z is the collision frequency and $p_r(T)$ is the reactivity. An appendix relates this result to transition state theory, by showing that

$$k_r(T) = k_{TST}(T)\kappa(T). \qquad (1.2)$$

Here $k_{TST}(T)$ is the transition state theory rate constant and the transmission coefficient $\kappa(T)$, $\kappa(T) \leq 1$, is the reactivity of the 'transition state' i.e. the fraction of collisions that reach the transition state and proceed to form products. Turned around, the expression $k_r(T) = Zp_r(T)$ can be regarded as employing transition state theory with a very very early transition state (so that $k_{TST}(T) = Z$) but with an exact account of the transmission coefficient.

Structure-reactivity relations are discussed in sections VI and VII. Starting with the definition of the Brønsted slope $\alpha$ $\alpha=-\partial \ln k_r(T)/\partial(\Delta G^\circ/RT)$ as the change in the rate constant with the free energy change of the reaction it is shown that for any Brønsted series one can rigorously express $k_r(T)$ as

$$k_r = Z\exp(-G_a/RT) \tag{1.3}$$

Here

$$G_a = \alpha\Delta G^\circ + G_a{}^\circ M(\alpha) \tag{1.4}$$

where Z is independent of $\Delta G^\circ$. $M(\alpha)$ is a function of $\alpha$ defined by

$$\partial M(\alpha)/\partial\alpha=-\Delta G^\circ/G_a^\circ$$

so that $\delta G_a = \alpha\delta\Delta G^\circ$ and $G_a^\circ$ is a parameter, with the dimensions of energy, which is characteristic of the reaction series. The monotonic increase of $\alpha$, and hence of $G_a$, with $\Delta G^\circ$ (i.e. the reactivity-selectivity principle) are shown to be valid for any Brønsted series. Section VII examines a simple model for the variation of free energy enroute from reagents to products. The concept of the inertia of chemical reactions, due to Evans and Polanyi[10] is shown to be sufficient to imply that the Brønsted slope $\alpha$ can be interpreted as the location of the free energy barrier to reaction (the Leffler postulate[12]) and that $\alpha$ shifts towards the products side as $\Delta G^\circ$ increases (the Hammond postulate[13]). The correlation[32] of barrier location with energy requirements and energy disposal of chemical reactions and with branching ratios is also discussed.

## II. A Thermodynamic Like Approach

The purpose of this section is to offer a derivation and interpretation of the expression

$$p_r = \exp(-G_a/RT) \tag{2.1}$$

for the reactivity in terms of a free energy $G_a$. Since (2.1) will be derived as an identity, valid irrespective of the detailed mechanism of the collision, it is of merit only if one can forge an independent route to $G_a$. Attempts in this direction are discussed in the subsequent sections of this paper and additional routes are under active examination.

The definition of reactivity to be introduced in this section is based on the following physical picture. For a bimolecular reaction, consider a large number of independent binary collisions (as in the case in a molecular beam or a chemiluminescence experiments[33]). The initial states of the colliding molecules are randomly selected from a system in thermal equilibrium at the temperature T. Not all such collisions necessarily lead to formation of products, as some may be non reactive. Reactivity is the fraction of such collisions that do lead to reaction. In this section, and then again in section III we are concerned with a thermodynamic-like characterisation, while a corresponding collision-theoretic analysis is provided in V. To make sure that the discussion retains an intuitive flavor, we shall use concepts appropriate to a quasiclassical description of the collision.[34,35]

In a computational study, the independent binary collisions are simulated by running N classical trajectories (where N is

a large number). The trajectories differ in their initial conditions and these are chosen to represent the distribution of the reactants.[34,36]

Thermal Reactants. To simulate a thermal distribution of the reagents one needs to run trajectories at different total energies. Since only a finite number of trajectories will be examined one needs to represent the distribution of total energy as a discrete histogram, such that there are $N_i$ trajectories with the (total) energy $E_i$. The average energy (per trajectory) is

$$\langle E\rangle=\Sigma_i N_i E_i/N. \qquad (2.2)$$

For a system at thermal equilibrium, $\langle E\rangle$ suffices to characterise the distribution of energy in the reactants. We show this explicitly, as a preliminary to the next stage of the argument.

Let there be $g_i$ distinct initial state of the energy $E_i$. The entropy of the initial ensemble is[4] (in units of the gas constant).

$$S = -\Sigma_i p_i \ln p_i + \Sigma_i p_i S_i \qquad (2.3)$$
$$= -\Sigma_i p_i \ln(p_i/g_i)$$

where $p_i = N_i/N$ and $S_i = \ln g_i$. If $p_i = g_i/N$ then $S = \ln N$. However, because of the constraint (2.2) it is not feasible to have $p_i=g_i/N$. Rather, one needs to determine the $p_i$'s subject to $\langle E\rangle=\Sigma_i E_i p_i$ and to $\Sigma_i p_i = 1$ by maximising the entropy. The result is well known[4]

$$p_i = g_i \exp(-E_i/RT)/Q \qquad (2.4)$$

where Q insures that the $p_i$'s are normalised,

$$Q = \Sigma_i g_i \exp(-E_i/RT) \qquad (2.5)$$

and the magnitude of T is adjusted to reproduce the given magnitude of E. In other words, T is that number that satisfies

$$\langle E\rangle=\Sigma_i E_i g_i \exp(-E_i/RT)/\Sigma_i g_i \exp(-E_i/RT) \equiv RT^2 \partial \ln Q/\partial T. \qquad (2.6)$$

Reactive Reactants. The equations of motion allow one to determine whether a given trajectory is reactive or not. Hence, if $N_{ri}$ is the number of reactive trajectories with the total energy $E_i$ and $N_{nri} = N_i - N_{ri}$ is the number of non reactive ones,

$$N\langle E\rangle = \sum_i N_{ri}E_i + \sum_i N_{nri}E_i \tag{2.7}$$

or

$$\langle E\rangle = p_r \langle E\rangle_r + p_{nr} \langle E\rangle_{nr} \tag{2.8}$$

where, as before $p_r = \Sigma_i N_{ri}/N$

and $\langle E\rangle_r$,

$$\langle E\rangle_r = \sum_i N_{ri}E_i/\sum_i N_{ri} \tag{2.9}$$

is the average energy of the reactive trajectories and similarly for $\langle E\rangle_{nr}$.

The central point is that not only the energy but also other thermodynamic functions, and in particular the entropy, can be resolved in a manner analogous to (2.8). To show this, it is convenient to define $x_{ri}$ as the fraction of the reactive trajectories with the energy $E_i$,

$$x_{ri} = N_{ri}/N_r \text{ or } \langle E\rangle_r = \sum_i x_{ri}E_i. \tag{2.10}$$

$$p_i = N_i/N = p_r x_{ri} + p_{nr} x_{nri} \tag{2.11}$$

The fraction $N_{ri}/N_i$, $(N_{ri}/N_i) = p_r x_{ri}/p_i$ (2.12)

has the interpretation of the fraction of trajectories from the state i which are reactive and will be denoted $g_{ri}/g_i$, so that

$$g_i = g_{ri} + g_{nri}. \tag{2.13}$$

It is important to note that even if we refine the interpretation of the index i, up to and including i being a complete specification of an initial quantum state, it would still be the case that $0 < g_{ri} < 1$ (rather than $g_{ri}$ being either unity of zero). The

reason is that a single quantum state is simulated by a group of classical trajectories (which differ in their initial classical conditions and while every single trajectory is either reactive or not, the different members of the group may behave differently).

Reactivity. The resolution (2.13) implies a similar resolution of the partition function

$$Q = Q_r + Q_{nr} \tag{2.14}$$

where

$$Q_r = \sum_i g_{ri} \exp(-E_i/RT) \tag{2.15}$$

and similarly for $Q_{nr}$. With this definition of $Q_r$ and the results $p_r x_{ri} = p_i g_{ri}/g_i$ and (2.12) we immediately obtain

$$\begin{aligned} p_r &= \sum_i p_r x_{ri} \\ &= \sum_i p_i (g_{ri}/g_i) \\ &= Q_r/Q \end{aligned} \tag{2.16}$$

This short derivation tends to stress that the result $p_r = Q_r/Q$ is indeed an identity but avoids a proper interpretation of $Q_r$. A longer, but more enlightening route is as follows: in terms of the reactivity, the expression (2.3) for the entropy can be brought to the form

$$S = -p_r \ln p_r - p_{nr} \ln p_{nr} + p_r S_r + p_{nr} S_{nr} \tag{2.17}$$

where

$$\begin{aligned} S_r &= -\sum_i x_{ri} \ln x_{ri} + \sum_i x_{ri} S_{ri} \\ &= -\sum_i x_{ri} \ln(x_{ri}/g_{ri}) \end{aligned} \tag{2.18}$$

with $S_{ri} = \ln g_{ri}$.

Using (2.17) and (2.18) one can now repeat the process of searching for the distribution of maximal entropy subject to the condition of given mean energy

$$\langle E \rangle = p_r \sum_i x_{ri} E_i + p_{nr} \sum_i x_{nri} E_i \tag{2.19}$$

and normalisation

$$p_r + p_{nr} = 1 \tag{2.20}$$

and

$$\sum_i x_{ri} = 1, \quad \sum_i x_{nri} = 1. \tag{2.21}$$

The result is

$$x_{ri} = g_{ri} \exp(-E_i/RT)/Q_r \tag{2.22}$$

$$Q_r = \sum_i g_{ri} \exp(-E_i/RT) \tag{2.15}$$

$$p_r = \exp(S_r - \langle E \rangle_r/RT)/Q \tag{2.23}$$

$$Q = \exp(S_r - \langle E \rangle_r/RT) + \exp(S_{nr} - \langle E \rangle_{nr}/RT) \tag{2.24}$$

Substituting (2.22) in (2.18) we have, using (2.15), that

$$S_r = \ln Q_r + \langle E \rangle_r/RT \tag{2.25}$$

and hence derive from (2.23) the desired results

$$p_r = Q_r/Q \tag{2.16}$$

$$Q = Q_r + Q_{nr} \tag{2.14}$$

For a system with a given value of the mean energy, it is the partition function that determines $p_r$. In terms of the free energy

$$G_r = -RT \ln Q_r \tag{2.26}$$

$$p_r = \exp[-(G_r - G)/RT] \tag{2.27}$$

$$= \exp[-G_a/RT]$$

$$= \exp[S_a - E_a/RT]$$

Here

$$G_a = G_r - G \tag{2.28}$$

$$E_a = \langle E \rangle_r - \langle E \rangle \tag{2.29}$$

and

$$S_a = S_r - S. \tag{2.30}$$

Pending further discussion below it should already be stated here that $S_r$ is not the information-theory entropy of the distribution of the reactive reactants (but is related to it via a Legendre transform).

Energy, Entropy and Work. To complete the discussion we note two additional implications. The first is the validity of a Gibbs-Helmholtz like theorem. To see this note that from (2.10) and (2.26)

$$\begin{aligned} \langle E \rangle_r &= RT^2 \partial \ln Q_r / \partial T \\ &= -T^2 \partial (G_r/T)/\partial T \end{aligned} \tag{2.31}$$

and hence that

$$S_r = -\partial G_r / \partial T. \tag{2.32}$$

In a more technical terminology we can write these identities as

$$S_r = \ln Q_r + T^2 \partial (\ln Q_r)/\partial T \tag{2.33}$$

showing that $S_r$ is the Legendre transform[37] of $\ln Q_r$. In practice these identities imply that $p_r$ has a well-defined temperature dependence

$$-\partial \ln p_r / \partial (1/T) \equiv RT^2 \partial \ln p_r / \partial T = E_a = \langle E \rangle_r - \langle E \rangle \tag{2.34}$$

It is important to note (as was first pointed out by Tolman[5,38]) that (2.34) is an exact relation and is by no means conditioned on $E_a$ being (nearly) temperature independent. Whatever the temperature dependence of $E_a$ may be, the relation (2.34) holds. The reason is that $S_a$ satisfies the Gibbs-Helmholtz like reaction

$$S_a = -\partial G_a / \partial T \tag{2.35}$$

or, equivalently,

$$\partial S_a/\partial T = T^{-1}\partial E_a/\partial T. \tag{2.36}$$

which is invoked in proving (2.34). If one defines $C_a = \partial E_a/\partial T$ as the difference in the specific heats between the reactive reactants and the reactants then

$$\partial S_a/\partial T = C_a/T \tag{2.37}$$

is the relation first noted by LaMer.[6]

The second point is that $-G_a = G-G_r$ does admit of an interpretation as the maximal work when a mole of reactive reactants (at the temperature T) is brought to thermal equilibrium (at the same temperature). The general approach to the computation of thermodynamic functions for systems in disequilibrium has been previously discussed.[29,31] Here we only need the final result. If $x_{ri}$ is the actual fraction of systems in the state i, and $p_{ri}$ is the thermal equilibrium fraction of systems in the state i at the temperature T, then the maximal work available in an isothermal process at the temperature T is, on statistical mechanical grounds[30],

$$RT\Sigma_i x_{ri}\ln(x_{ri}/p_{ri}) = -G_a \tag{2.38}$$

where the equality (2.1) follows when one notes that $p_{ri} = p_r x_{ri}$. If one prefers purely thermodynamic reasoning, the maximal work under isothermal conditions is[39]

$$(\langle E\rangle-\langle E\rangle_r)-RT(S-S_r)= -(E_a-RTS_a) = -G_a \tag{2.39}$$

Of course, the simplicity of (2.39) is misleading for without information theory $S_r$ is not easily interpreted.

Summary. From a purely algebraic point of view what was shown in this section is that any quantity which is an average over a thermal distribution can be expressed as a ratio of two partition functions. To reiterate the general nature of this result consider some arbitrary dimensionless quantity B, whose magnitude in the state i is $B_i$. The thermal average, $\langle B \rangle$ of B is

$$\langle B \rangle = \sum_i p_i B_i. \tag{2.40}$$

It follows by explicit differentiation of (2.40) that

$$RT^2 \partial \langle B \rangle / \partial T = \langle BE \rangle - \langle B \rangle \langle E \rangle \tag{2.41}$$

and hence that an 'activation energy' can always be defined

$$RT^2 \partial \ln \langle B \rangle / \partial T = \frac{\langle BE \rangle}{\langle B \rangle} - \langle E \rangle = \langle E \rangle_B - \langle E \rangle \tag{2.42}$$

where $\langle E \rangle_B$ is the average energy of the normalised distribution

$$b_i = g_i B_i \exp(-E_i/RT)/Q_B \tag{2.43}$$

with

$$Q_B = \sum_i g_i B_i \exp(-E_i/RT). \tag{2.44}$$

Recalling that $p_i = g_i \exp(-E_i/RT)/Q$ we have from (2.40) and (2.44)

$$\langle B \rangle = Q_B/Q \tag{2.45}$$

The expression of the reactivity in the form (2.16) is thus a mathematical identity. Even if the reactants were state selected, one could still obtain a suitably generalised similar result. The merit of the observation is thus entirely in the question of whether it can be used to any advantage in extending our understanding of chemical reactivity.

III. Cycles.

The ultimate test of the concept of free energy of the reactive reactants, $G_r=-RT\ln Q_r$ , is whether it can be employed to construct thermodynamic cycles. The typical cycle to be considered will be a work cycle in which a system coupled to a heat bath is restored to its initial state. The second law implies that such a process cannot deliver any net work. We shall show that the definition of $G_r$ is consistent with this implication of the second law, and explore a few cycles of possible interest. A general demonstration that thermodynamic cycles can be constructed also for systems in disequilibrium has been given elsewhere.[29]

Reactive Reactants. The simplest possible cycle is one where a mole of reactants (at equilibrium with a heat bath) is separated into $p_r$ moles of reactive reactants and $p_{nr}=1-p_r$ moles of non-reactive reactants. The work of separation must then be equal to the maximal work that can be recovered when the two subsystems are allowed to return to equilibrium (in an isothermal process at the same temperature T). The proof is an immediate implication of our basic conclusion (cf. (2.14)) $Q=Q_r+Q_{nr}$ . Since $p_r=Q_r/Q$ and since the work available from $p_r$ moles of reactive reactants (cf. (2.38)) is $p_r(G_r-G)$ and similarly for the non-reactive reactants, it follows that

$$W_{sep}\equiv RT[-p_r\ln p_r-p_{nr}\ln p_{nr}]=p_r(G_r-G)+p_{nr}(G_{nr}-G). \qquad (3.1)$$

Nascent Products. To elaborate on the previous cycle, let the $p_r$ moles of reactive reactants undergo their single collision producing $p_r$ moles of nascent, unrelaxed, products. Work is then obtained as the nascent products are allowed to relax, isothermally,

to equilibrium, producing $p_r$ moles of thermal products. To convert these into thermal reactants requires $-p_r\Delta G^o$ units of work. The net work delivered by the cycle is

$$W = -W_{sep} + W_{na} + W_n + p_r\Delta G^o. \tag{3.2}$$

Here $W_{na} = p_{nr}(G_{nr} - G)$ is the work available from the $p_{nr}$ moles of nonreactive reactants that are brought back to equilibrium and $W_n$ is the work available form the $p_r$ moles of nascent products.

To show that $W \equiv 0$ one must show that $W_n + p_r\Delta G^o = W_r = p_r(G_r - G)$ where $W_r$ is the work available from $p_r$ moles of reactive reactants, for then, using (3.1), $W \equiv 0$. Since $\Delta G^o = (G' - G)$ where G' is the free energy of the thermal products, we need to show that $G_n$, the free energy of the nascent products ($W_n = p_r(G_n - G')$) is given by

$$G_n = G_r \ , \tag{3.3}$$

i.e., the free energy of the nascent products equals that of the reactive reactants. Of course, one can argue that (3.3) must be the case, as otherwise the second law will be violated.[40] In other words, if (3.3) fails, one could employ a velocity selector (or any other device for selecting more reactive molecules and thereby affecting at least a partial separation) to produce work from heat, on a continous basis. One can, however, prove (3.3) without appeal to Maxwell's demon, as follows:

To prove (3.3) one needs to invoke detailed balance twice. It is important to note that since we are dealing here with isolated binary collisions, detailed balance follows[41] from microscopic re-

versibility and does not depend on invoking the second law in its proof. The first implication of detailed balance is that

$$G_r = G'_r \tag{3.4}$$

i.e., that the free energy of the reactive reactants in the forward reaction equals that of the reactive reactants in the reversed reaction. A simple short proof is based on

$$(Q'/Q) = K(T) = p_r/p'_r \tag{3.5}$$

where $K(T)$ is the equilibrium constant. Hence $Q_r = Q'_r$ and (3.4) follows. The second implication of detailed balance is that

$$G_n = G'_r \tag{3.6}$$

i.e., that the free energy of the nascent products of the forward reaction equals the free energy of the reactive reactants in the reversed reaction. The proof is immediate, since detailed balance implies[41] that the two distributions are identical. Combining (3.6) and (3.4) we have (3.3) and hence conclude that $W = 0$ (cf. (3.2)).

There are altogether four distributions, two on either side of the barrier. The two on the same side (reactive reactants and nascent products of the same species but of opposite reactions) are identical and all four have the same free energy. It is this last conclusion which enables one to incorporate kinetic concepts into thermodynamic-like cycles.

Energy Disposal. The free energy of a mole of thermal reactants exceeds that of a mole of thermal products by $G - G' = -\Delta G^{o}$. On the other hand, the free energy of a mole of nascent products exceeds that of a mole of thermal products by

$$G_n - G' = G_r - G + G - G' = G_a - \Delta G^{o}. \tag{3.7}$$

If a reaction does not take place spontaneously, it follows that $G_n \equiv G_r' > G'$. It takes work to drive the reaction and the excess of the work required ($G_a$) over the minimal work required to form the thermal products ($\Delta G^{o}$) appears as the work available from the nascent products.

The inertia, $G_a - \Delta G^{o}$, is thus the work available from the nascent products as these relax to thermal equilibrium. Given two reactions at the same $\Delta G^{o}$, the one leading to more 'work-rich' products will have a higher $G_a$ and hence a lower reactivity. For a given $\Delta G^{o}$, specificity of energy disposal as measured by $G_n - G'$ increases as the inertia increases and hence as the reactivity diminishes.[42]

What is still missing is the dependence of the inertia on $\Delta G^{o}$. For an exoergic reaction, where $-\Delta G^{o} > 0$, it follows from (3.7) that $G_n = G_r > G = G' - \Delta G^{o}$, i.e., that the excess free energy of the nascent products ($G_n - G'$) exceeds $-\Delta G^{o}$. However, for an endothermic reaction, where $-\Delta G^{o} < 0$, (3.7) provides no useful bound. What we need is the dependence of $G_n - G'$ on $\Delta G$, i.e., what is the fraction of $G_a$ that ends up as excess free energy of the nascent products. Any cycle that we were able to come up

with, turned out to be equivalent to (3.7) and hence failed to provide an answer. The question will thus have to wait till section VI where the conclusion will be that $G_n - G' \simeq -\Delta G^o$ (i.e., $G_a \simeq 0$) as $-\Delta G^o >> RT$ while $G'_n - G' \simeq 0$ (i.e., $G_a \simeq \Delta G^o$) as $\Delta G^o >> RT$.

Reactivity as an Equilibrium Constant. The introduction of cycles enables one to regard $p_r(T) = Q_r/Q$ as the equilibrium constant between the thermal reagents and the reactive reagents, say

$$Cl + HI \rightleftarrows (Cl + HI)_r.$$

As a check we verify that it satisfies the usual product rule for a sequence of equilibria. Consider say

$$Cl + HI \rightleftharpoons ClH + I.$$

It can be broken into the following sequential stages:

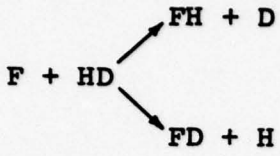
$$Cl + HI \rightleftharpoons (Cl + HI)_r \rightleftharpoons (ClH + I)_n \rightleftharpoons ClH + I.$$

The respective equilibrium constants are $p_r(T)$, unity (since $G_r = G_n$) and $1/p'_r(T)$. Indeed since $Q_n = Q_r$ ,

$$K(T) = p_r(T) \cdot 1 \cdot (1/p'_r(T)). \qquad (3.8)$$

As another consistency check, it follows that reactive reactants have a unit reactivity, as they should.

Branching Ratios. Consider first an intramolecular branching ratio as, say, for the F + HD reaction[43]



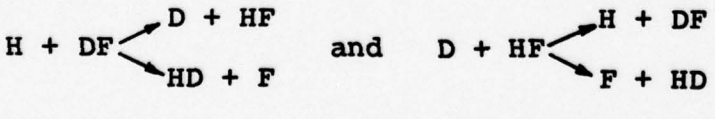

The relative rate of H vs. D abstraction, starting with thermal reagents, is given by

$$-RT\ln\Gamma \equiv -RT\ln(p_H/p_D) = G_n(H) - G_n(D) \tag{3.9}$$

where $G_n(X)$ is the free energy of the nascent products in the X abstraction path. $\Gamma$ is thus the ratio of the partition function of the nascent products (or of the reactive reactants), $\Gamma = Q_n(H)/Q_n(D)$. Alternatively, if $K_n(T)$ is the equilibrium constant between F + HD and say $(FD + H)_n$ (i.e., $K_n(T) = p_D(T)$) then

$$\log \Gamma = \Delta pK_n. \tag{3.10}$$

An explicit cycle corresponding to the identity (3.10) is easily constructed. Consider the two reactions




whose branching ratios (for thermal reagents) will be denoted by $\Gamma_H$ and $\Gamma_D$ respectively. Then (3.10) is equivalent to

$$\Gamma = \Gamma_H/\Gamma_D \ . \tag{3.11}$$

The identity (3.10) remains equally valid also for intramolecular comparisons. A very simple example is a comparison of the rates of forward and reversed reactions. Using the cycle

$$\begin{array}{ccc} A + BC & \rightarrow & (AB + C)_n \\ \uparrow & & \downarrow \\ (A + BC)_n & \leftarrow & AB + C \end{array}$$

and (3.4), we recover the well known result $k_r/k'_r = K$. More elaborate cycles can also be devised. An alternative direction is, as in the intramolecular branching problem,[43] to relate the differences in reactivity to the energy disposal (or energy consumption). Two worthwhile examples are[44]

$$Cl + HI \rightarrow ClH + I \text{ vs. } Cl + HBr \rightarrow ClH + Br$$

and[42]

$$H + O_2N \rightarrow HO + ON \text{ vs. } H + O_3 \rightarrow HO + O_2 .$$

For both examples, the first reaction is over an order of magnitude more reactive than the second. In section VI, where the dependence of $G_a$ on $\Delta G^o$ is explored, it will be found possible to obtain explicit results (cf. figure 3 below) for the intramolecular branching ratio.

## IV. The Partition Function

A direct computation of the reactivity requires the determination of the partition function $Q_r$. To do so we need the 'degeneracies' $g_{ri}$ of the reactive reactants (cf. (2.22)) and these are only available from a detailed microscopic (experimental or computational) study. This section explores two theoretical techniques that may prove useful for determining $Q_r$ in terms of macroscopic observables. The first is the use of the Legendre transform.[37] This venerable procedure will be invoked below in the discussion of free energy relations. The second is the use of bounds.

The Legendre Transform. The partition function is a function of the temperature. The Legendre transform replaces it by a different function, whose variable is $-\partial \ln Q_r/\partial(1/T)$ such that both functions provide precisely the same information.[37] Using (2.33) the Legendre transform of $\ln Q_r$ with respect $1/T$ is $S_r$

$$S_r = \ln Q_r - (1/T)[-\partial \ln Q_r/\partial(1/T)] \qquad (4.1)$$

Knowing $S_r$ as a function of $\langle E \rangle_r$ is thus equivalent to knowing $Q_r$ as a function of T. Indeed, the determination of $S_r$ by integrating (2.36) was essentially the suggestion of LaMer.[6] Unfortunately, the determination of $Q_r$ via the measured T-dependence of the activation energy is not easy to implement, due to experimental difficulties in detecting small changes in $E_a$. Similar practical difficulties arise in another attempt to invert a Legendre transform of $Q_r$, to be discussed below. Much earlier, such difficulties in the determination of Q have given rise to the formulation of the Nernst heat theorem. There may well be a lesson here too, but

its significance is not clear at the moment.[22,23]

Energy Consumption. $Q_r$ may well depend on additional variables beside the temperature via its dependence on the $g_{ri}$'s. The ratio $g_{ri}/g_i$ is, by construction, the probability of reaction for a state in the group i and the observation that $g_{ri}$ is not necessarily proportional to $g_i$ (i.e. $g_{ri}/g_i \neq p_r$) gives rise to the concept of 'selectivity of energy consumption'. To allow also for the possibility that the probability of reaction depends not only on the total energy but also on the partition of the total into the different degrees of freedom, we shall regard i as an index of a detailed state selection for the reactions. To bring this aspect into the open it is convenient to introduce S[x],

$$S[x] = -\sum_i x_{ri} \ln(x_{ri}/g_i), \tag{4.2}$$

the entropy of the distribution of the reactive reactants, regarded as a distribution of quantum states. S[x] is maximal when all states at a given energy react with the same probability.[4] From their respective definitions,

$$S[x] = S_r - \sum_i x_{ri} \ln(g_{ri}/g_i) \tag{4.3}$$

and since $g_{ri} \leqslant g_i$, $-\ln(g_{ri}/g_i) \geqslant 0$ with equality if $p_r = 1$ and so $S[x] \geqslant S_r$ with equality when $p_r = 1$. It follows that

$$p_r \leqslant \exp\{S[x] - \langle E \rangle_r / RT\}/Q. \tag{4.4}$$

Two reactions, with the same energy of activation, may thus differ in their reactivity because of differences in their selectivity of energy consumption. As the selectivity increases, S[x] diminishes and so does the reactivity.[42] The origin of this 'selectivity-reactivity' principle is indeed trivial. Since at most all the

trajectories in the group can be reactive, $g_{ri} \leqslant g_r$. Since selectivity implies that $g_{ri} \neq p_r g_i$ it follows that a measure of selectivity should vanish when $g_{ri} = p_r g_i$ and otherwise be always positive. Using (2.12), the 'local' deviance of $g_{ri}$ from $p_r g_i$ is $(g_{ri}/p_r g_i)=(x_{ri}/p_i)$. An 'integral' measure of selectivity is thus given by $q_r$ defined as

$$\ln q_r = -\sum_i x_{ri} \ln(x_{ri}/p_i) \qquad (4.5)$$

where, using the Gibbs-Boltzmann inequality[4], $\ln q_r \leqslant 0$ with equality if and only if $g_{ri} = g_i p_r$. However, using (2.22)

$$\ln q_r = S[x]-(\langle E\rangle_r/RT)-\ln Q \qquad (4.6)$$

or

$$q_r = \exp\{S[x]-\langle E\rangle_r/RT\}/Q \qquad (4.7)$$

so that $p_r \leqslant q_r$. This bound on the reactivity will be further discussed below.

A Tale of Two Entropies. For a molecular system, entropy is a measure of the uncertainty as to the actual quantum state of the system[45]. The magnitude of the entropy will thus depend on the amount of information already available on the system. Any input that can be used to eliminate some quantum states as possible states will thus tend to reduce the entropy. The inequality $S[x] \geqslant S_r$ is a quantitative statement of such consideration $S[x]$ is the uncertainty given that the distribution of quantum states is $x_{ri}$. The choice is then among all possible states of the reactants. The work required for such a search is[29,30] $RT\ln q_r$. $S_r$ is the uncertainty given that the distribution is $x_{ri}$ and that the choice is restricted to the reactive reactants. Since

$g_{ri} \leq g_i$, the number of possible quantum states is reduced, $S_r \leq S[x]$ and the work required for such a search, $RT\ln p_r$, is lower. The difference between the two entropies is, in a sense, a quantal effect. In the classical limit we can take i to index the initial conditions, whence $g_{ri}$ is either zero or unity, while $g_i$ is unity. When $g_{ri} = 0$ $x_{ri}$ also vanishes, so that the two entropies agree, as the search is precisely over the same range of possible contenders. The same conclusion is quantitatively evident from (4.3). Of course, the need for two entropies is partly of our own making, for having introduced the distribution of reactive reactants. In general, it is S[x] which has the conventional structure of an entropy, for it is the missing information of the distribution $x_{ri}$, given only macroscopic information on that distribution. It is therefore of interest to note that the $S_r$ can be obtained as a Legendre transform S[x].

Consider the simplest situation where besides $\langle E \rangle_r$, the only macroscopic input required to characterise the distribution of reactive reactants is the magnitude of $\langle C \rangle_r = \sum_i x_{ri} C_i$ where $C_i$ is a property which depends on i. Then[46]

$$x_{ri} = g_i \exp[-(E_i/RT) - \gamma C_i]/Q_r \tag{4.8}$$

where the magnitude of $\gamma$ is adjusted so that the distribution $x_{ri}$ is consistent with the value of $\langle C \rangle_r$. For that value of $\gamma$,

$$\langle C \rangle_r = -\partial \ln Q_r / \partial \gamma. \tag{4.9}$$

Since $g_{ri} = g_i \exp(-\gamma C_i)$, it follows that $\gamma C_i \geq 0$ and $\gamma \langle C \rangle_r \geq 0$ with equality if $g_{ri} = g_i$.

The Legendre transform of $\ln Q_r$ with respect 1/T is still $S_r$, but the Legendre transform with respect both 1/T and $\gamma$ is

$$S[x] = \ln Q - (1/T)\partial \ln Q_r/\partial(1/T) - \gamma \partial \ln Q_r/\partial\gamma \qquad (4.10)$$
$$= \ln Q + \langle E\rangle_r/RT + \gamma\langle C\rangle_r$$
$$= S_r + \gamma\langle C\rangle_r$$

Here $S[x]$ is a function of $\langle E\rangle_r$ and $\langle C\rangle_r$, whereas $S_r$ is a function of $\langle E\rangle_r$ and of $\gamma$. Since $\gamma = \partial S[x]/\partial\langle C\rangle_r$, $S_r$ and $S[x]$ are also a pair of Legendre transforms

$$S_r = S[x] - \langle C\rangle_r \frac{\partial S[x]}{\partial \langle C\rangle_r} \qquad (4.11)$$

Bounds. The upper bound (4.4) on the reactivity was derived from the observation that not all trajectories are necessarily reactive. This suggests a generalisation. There is a range of intermediate distributions between $p_i$ ('all trajectories that originate from the reactants') and $x_{ri}$ ('reactive trajectories'). For example, all trajectories that originate from the reactants and that cross any dividing surface which separates the reagents from the products.[47-50] If the surface is close to the reactants, the distribution is close to $p_i$ while if it is close to the products, it is close to $x_{ri}$. If there is a 'surface of no return' such that any trajectory which crosses the surface proceeds to form products, then the distribution for that surface is precisely $x_{ri}$. In mathematical terms, we argue that since $g_{ri} \leqslant g_i$ one can always define $g_{+i}$ such that

$$g_{ri} \leqslant g_{+i} \leqslant g_i \qquad (4.12)$$

Multiplying every term in (4.12) by the (positive) number $\exp(-E_i/RT)$ and summing over i,

$$Q_r \leqslant Q_+ \leqslant Q \qquad (4.13)$$

or

$$p_r \leqslant p_+ \equiv Q_+/Q \qquad (4.14)$$

The physical argument is, of course, the one employed in the variational theory of reaction rates[47-49], and enables one to endow the mathematical result (4.14) with a physical interpretation. A mathematical proof of the bound is also available using the Gibbs-Boltzmann inequality as in (4.4).

A lower bound for the partition function is also readily derived, by a simple interchange of $x_{ri}$ and $p_i$ in the Gibbs-Boltzmann inequality

$$\begin{aligned} \sum_i p_i \ln(p_i/x_{ri}) &= -S[p] - \sum_i p_i \ln(x_{ri}/g_i) \\ &= -S[p] + \langle E\rangle/RT + \gamma\langle C\rangle + \ln Q_r \\ &= \ln Q_r - \ln Q + \gamma\langle C\rangle \geqslant 0 \end{aligned} \tag{4.15}$$

or $\ln p_r \geqslant -\gamma\langle C\rangle$. The two inequalities brought together are

$$\exp[-\gamma\langle C\rangle] \leqslant p_r \leqslant \exp\,[-\gamma\langle C\rangle_r] \tag{4.16}$$

where $\langle C\rangle$ is the average value of $C_i$ (cf. (4.8)) over the distribution of thermal reactants.

The link between the upper bound in (4.14) and (4.16) is provided by noting that the essential inequality is $Q_r \leqslant Q\exp[-\gamma\langle C\rangle_r]$ and that using (4.12) one can also write $Q_r \leqslant Q_+\exp[-\gamma(\langle C\rangle_r - \langle C^+\rangle_r)]$ where $\gamma C_i^+ = -\ln(g_{+i}/g_i) \leqslant \gamma C_i$, so that $Q_r \leqslant Q_+$ and especially obtains when there is a surface of no return so that $C_i^+ = C_i$. A similar trick is available for the lower bound, $Q_r \geqslant Q_+\exp[-\gamma(\langle C\rangle_+ - \langle C^+\rangle_+)]$ where the + subscript denotes an average over the distribution $g_{+i}\exp(-E_i/RT)/Q_+$. Since $\gamma\langle C\rangle_+ \geqslant 0$, one can obtain a lower bound

$$p_r \geqslant (Q_+/Q)\exp(\gamma\langle C^+\rangle_+) \tag{4.17}$$

which is complementary to the upper bound (4.14). Since $\gamma C_i^+ = -\ln(g_{+i}/g_i)$, the bound (4.17) can be computed when $Q_+$ is available. The bound is not perfect, since it is always a bound rather than

an equality, but it can be improved upon.

## V. Dynamics

This section introduces the concept of reactivity on collision-theoretic grounds. As in section II, a classical trajectory computation point of view is employed.

Let n denote the set of classical variables corresponding to the quantal interval quantum numbers, $E_T$ the translational energy of the collision and b the impact parameter, whose range is taken from zero to some maximal value B. The number of trajectories used in the range b to b + db is related to the total number run by

$$N(n,E_T,b)db = (2\pi bdb/\pi B^2)N(n,E_T). \tag{5.1}$$

Here $N(n,E_T)dE_T$ the number of trajectories used for translational energy in the range $E_T$, $E_T + dE_T$ with specified n. The number of reactive trajectories for an impact parameter in the range b, b + db is $N_r(n,E_T,b)db$. The reactivity at a given b (sometimes called[33] 'the opacity function') is

$$P(b) = N_r(n,E_Tb)/N(n,E_T,b), \tag{5.2}$$

and the number of reactive trajectories for $E_T$ in the range $E_T$, $E_T + dE_T$ and given n is a sum (i.e., integral) over all possible values of b

$$N_r(n,E_T) = \int_0^B dbN_r(n,E_T,b). \tag{5.3}$$

B is chosen such that the integrand in (5.3) is effectively zero for b > B.

The reaction cross section, defined by[33]

$$\sigma(n,E_T) = 2\pi \int_0^B bP(b)db \tag{5.4}$$

can now be rewritten, using (5.2) and (5.1) as[51]

$$\sigma(n,E_T) = \pi B^2 \int_0^B N_r(n,E_T,b)db/N(n,E_T) = \pi B^2 N_r(n,E_T)/N(n,E_T) \tag{5.5}$$

i.e., as $\pi B^2$ times the reactivity at a given $E_T$. A similar 'Monte-Carlo' integration can also be used to relate the rate constant and the reactivity at the temperature T. To do so we sample trajectories at different translational energies by

$$N(n,E_T) = Z(E_T)f(E_T)N(n)/Z \tag{5.6}$$

Here N(n) is the number of trajectories employed for reactants in the internal state n. $f(E_T)dE_T$ is the fraction of systems at thermal equilibrium with translational energy in the range $E_T$ ,$E_T + dE_T$

$$f(E_T) = \rho_T(E_T)\ \exp(-E_T/RT)/Q_t \tag{5.7}$$

where $\rho_T(E_T)$ is the translational density of states and $Q_t$ is the translational partition function. $Z(E_T)$ is the collision frequency at the translational energy $E_T$, $Z(E_T) = \pi B^2 \underline{v}$, where $\underline{v}$ is the relative velocity and Z is the thermal average of $Z(E_T)$. If B is independent of $E_T$, $Z = \pi B^2 \langle \underline{v} \rangle$.

The reaction rate constant is

$$k(n,T) = \int_0^\infty f(E_T)\underline{v}\sigma(n,E_T)dE_T \tag{5.8}$$

and using (5.5) and (5.6),

$$k(n,T) = \int_0^\infty dE_T f(E_T) Z(E_T) [N_r(n,E_T)/N(n,E_T)] = Z[N_r(n)/N(n)]. \tag{5.9}$$

Here $N_r(n)$ is the number of reactive trajectories

$$N_r(n) = \int_0^\infty dE_T N_r(n,E_T), \tag{5.10}$$

starting with the internal state n.

The final stage is to obtain the thermal rate constant

$$k(T) = \sum_n [N(n)/N]k(n,T) = Z(N_r/N) \tag{5.11}$$

where $N_r = \Sigma_n N_r(n)$ is the total number of reactive trajectories.

The careful reader will note that Z, the collision rate, depends on B, whose numerical magnitude has not been precisely assigned. This indeed is a weakness of classical mechanics. It is unable to specify a B beyond which there are no collisions.[33] Even so, the magnitude of k(T) is independent of the choice made for B (provided only it is large enough, and that N is large). The reason is that as can be inferred from (5.1), it is only the ratio $B^2/N$ that matters and only this ratio appears in k(T).

The Sampling Procedure. It is essential to note that by running enough trajectories (i.e., in the limit of large N) one obtains the correct (quasi-classical) magnitude of the rate constant for any reasonable sampling strategy of the initial states. The reason is obvious. If we accentuate the role of any particular state, the number of reactive trajectories originating from that state will also increase, and the reactivity (cf. (5.2) or (5.5)) will remain unchanged, provided N is large. Thus, while the functional form for the rate constant (as the collision frequency times the fraction of trajectories that do react) does depend on a particular choice of the sampling procedure, its magnitude computed using (5.8) is independent of this choice. In other words, the ratio $N_r(n,E)/N(n,E)$ (which is the analogue of $(N_{ri}/N_i) = g_{ri}/g_i$ of section II) is independent of the sampling procedure. A different sampling procedure is employed in the Appendix to rederive the present results and to bring them to the form

$$k(T) = \kappa(T) k_{TST}(T) \tag{5.12}$$

Here $k_{TST}(T)$ is the transition state theory rate constant and K(T)

$$\kappa(T) = [N_r/N_+] \leq 1 \tag{5.13}$$

is the transmission coefficient. $N_+$ is the number of trajectories that originate from the reagents and that cross the dividing surface from reagents to products and hence is an upper bound for $N_r$. As is already evident and will be further discussed in the appendix, $\kappa(T)$ can be regarded as the reactivity of the transition state.

## VI. The Brønsted Series

The variation of the magnitude of the reaction rate constant with structural modifications in the reagents is, in principle, contained in the two partition functions $Q_r$ and Q. In practice, equilibrium statistical mechanics accounts for the variations in Q, but we have no obvious route (except for cycles) to $Q_r$. A simple approach, based on the concept of a Brønsted series, is examined in this section, where the point of view is strictly operational. An interpretation of the results in terms of a model is considered in the next section.

The Brønsted Coefficient. The Brønsted coefficient is a measure of the change in the reaction rate constant due to changes in the free energy of the reaction

$$\alpha = \partial \ln k_r(T)/\partial \ln K(T) = -\partial \ln k_r(T)/\partial(\Delta G^o/RT). \qquad (6.1)$$

The mathematical definition is given a physical interpretation by the assumption that in a series of 'similar' reactions, structural changes in the reactants change the reaction rate primarily via the change in the $\Delta G^o$ of the process. This interpretation is saved from being a circular one ('a series of similar reactions is one for which the Brønsted relation is a useful measure', 'the Brønsted slope is a useful measure for a series of similar reactions') by the empirical observation that there are indeed many known examples of the utility of the concept.[2,18,28] The very same observation is valid of course in general ('The phase rule is valid for a heterogenous system in equilibrium', 'a heterogenous system is in equilibrium if the phase rule obtains'). The only logical grounds for

further enquiry are thus that one would like to link the definition to other, possibly more general, physico-chemical concepts and, in so doing, identify the implications of deviant behavior. In other words, one would like to invoke the concept as a yardstick in the same fashion that the phase rule is used to decide whether geological samples (or meteorites) are indeed in equilibrium.

The 'Entropy' Term. For small variations in $\Delta G^{o}$, the variation in the rate constant can be expressed as[11]

$$\delta \ln k_r = -\alpha \delta (\Delta G^{o}/RT) \tag{6.2}$$

However, if $\alpha$ is not independent of $\Delta G^{o}$, the application of (6.2) is limited (say to changes in $\Delta G^{o}$ due to external parameters, e.g., pressure). In particular, structural modifications such that the change in $\Delta G^{o}$ exceeds RT cannot be discussed. An alternative approach is to explicitly integrate (6.1), holding all variables except $\Delta G^{o}$ constant. To allow for a possible $\Delta G^{o}$ dependence of $\alpha$, (6.2) is written as

$$d\ln k_r(T) = -d(\alpha \Delta G^{o}/RT) + (\Delta G^{o}/RT)\, d\alpha \tag{6.3}$$

or

$$\ln k_r(T) = \ln Z - \alpha(\Delta G^{o}/RT) - (G_a^{o}/RT) M(\alpha) \tag{6.4}$$

Here lnZ is the integration constant, which is thus independent of $\alpha$ while $M(\alpha)$ is a dimensionless function of $\alpha$, defined by comparing (6.4) to (6.3), as

$$(G_a^{o}/RT)\, \partial M(\alpha)/\partial \alpha = -\Delta G^{o}/RT. \tag{6.5}$$

In other words, $G_a^o M(\alpha)$ is defined as the integral of $\Delta G^o d\alpha$. $G_a^o$ has the dimension of free energy and, by construction, is independent of $\alpha$. A Brønsted series is characterized by a given value of $G_a^o$. For such a series one can explicitly construct the function $M(\alpha)$, given the magnitude of the reaction rate for different members of the series. (This serves to determine $\alpha$ as a function of $\Delta G^o$, and equation (6.5) can then be explicitly integrated.) The magnitude of $G_a^o$ can be fixed, say by the convention that at the stationary point of $M(\alpha)$, (that is, at $G_a^o \partial M/\partial\alpha = -\Delta G^o = 0$), $G_a^o = G_a$.

The representation of the reaction rate constant as

$$k(T) = Z \exp(-G_a/RT) \tag{6.6}$$

$$G_a = \alpha\Delta G^o + G_a^o M(\alpha) \tag{6.7}$$

with Z independent of $\Delta G^o$ is thus a mathematical statement, equivalent to the original definition of $\alpha$. Given equation (6.2), there always exists a function $G_a^o M(\alpha)$ such that the $\Delta G^o$-dependence of the rate constant can be stated in the form (6.6) with $G_a$ having the form (6.7), and using the definition (6.5), satisfying the Legendre transform relations

$$(G_a/G_a^o) = M(\alpha) - \alpha(\partial M/\partial\alpha) \tag{6.8}$$

or

$$M(\alpha) = (G_a/G_a^o) - \Delta G^o[\partial(G_a/G_a^o)/\partial\Delta G^o] \tag{6.9}$$

The specification of the $\alpha$-dependence of M is thus strictly equivalent to the determination of $G_a$ as a function of $\Delta G^o$. (An

explicit example is discussed later.) For small variations in $\Delta G^{o}$, the result (6.2) remains valid for any function $M(\alpha)$ that satisfies (6.5) or, equivalently, (6.8), but only if $G_a^{o} >> \Delta G^{o}$ can $\alpha$ be taken to be independent of G.

Detailed Balance. To inject some physics into the discussion, consider the implication of detailed balance. For a given elementary reaction, the forward and reverse rate constants are related by

$$k(T)/k'(T) = K(T) = \exp(-\Delta G^{o}/RT). \tag{6.10}$$

Since Z (cf. equation (6.6)) is independent of $\Delta G^{o}$, it can be taken to be the same for the forward and reverse reaction (always subject to the assumption that these belong to the same Brønsted series). Hence the Brønsted slope for the reversed reaction, (whose standard free energy change is $-\Delta G^{o}$, where $\Delta G^{o}$ is the standard free energy change in the forward reaction), is

$$\alpha' = -\partial \ln k'(T)/\partial(-\Delta G^{o}/RT) = -\partial \ln K(T)/\partial(\Delta G^{o}/RT) + \partial \ln k(T)/\partial(\Delta G^{o}/RT)$$
$$= 1 - \alpha$$

or

$$\alpha + \alpha' = 1. \tag{6.12}$$

Furthermore, since (6.10) implies that

$$G_a(\alpha) - G_a(\alpha') = \Delta G^{o} \tag{6.13}$$

and since $G_a^{o}$ is independent of $\Delta G^{o}$, it follows from (6.7) that

$M(\alpha) - M(\alpha') = 0$, or using (6.12),

$$M(\alpha) = M(1 - \alpha). \tag{6.14}$$

As $\alpha$ varies over the range zero to one, $M(\alpha)$ is a symmetric function of its argument. Indeed, we know from (6.5) that $M(\alpha)$ has a stationary point ($\partial M(\alpha)/\partial\alpha = 0$) for that value of $\alpha$ that corresponds to $\Delta G^{o} = 0$ (a 'symmetric' reaction). The symmetry of $M(\alpha)$ implies that the maximum occurs at $\alpha = 1/2$. On the other hand, taking the derivative of both sides of (6.5) with respect to $\Delta G^{o}/RT$, we conclude that

$$(G_a^{o}/RT)[\partial^2 M(\alpha)/\partial\alpha^2][\partial\alpha/\partial(\Delta G^{o}/RT)] = -1. \tag{6.15}$$

The two derivatives in (6.15) are thus necessarily of opposite sign. The result is again very much expected since it is equivalent to the statement that the second derivatives of $M(\alpha)$ and of $G_a(\Delta G^{o})$, which are a Legendre transform pair, are of opposite signs. Hence, if $M(\alpha)$ has a maximum at $\alpha = 1/2$, $\alpha$ is a montonically increasing function of $\Delta G^{o}$.

The monotonic variation of $\alpha$ with $\Delta G^{o}$ holds for any Brønsted series. Any failure of this result is thus evidence that one is not comparing reactions of the same series. All that remains is to determine whether $\alpha$ increases or decreases as $\Delta G^{o}$ is increased.

The Inertia of Chemical Reactions. This is about as far as one can go on general grounds. A small infusion of chemical common sense (or empiricism) is however quite beneficial at this point. The essential idea is due to Evans and Polanyi[10,11], who pointed

out that the inertia of chemical reactions exceeds their thermodynamic driving force. In mathematical terms, this means that at any magnitude of $\Delta G^o$ the function $G_a(\Delta G^o)$ is everywhere above its tangent at that point, i.e., $G_a(\Delta G^o)$ is a concave function of $\Delta G$ as is evident in figure 1. In more direct terms, consider a symmetric ($\Delta G^o = 0$) reaction and another reaction of the same family with a small but finite $\Delta G^o$. Then, if $(\Delta G^o/RT) > 0$, $G_a$ increases in excess of $\Delta G^o/RT$ and if $(\Delta G^o/RT) < 0$, $G_a$ decreases by less than $-\Delta G^o/RT$. These two equivalent statements are that $\partial^2 G_a/\partial(\Delta G^o)^2 > 0$ and that $\partial^2 M/\partial\alpha^2 < 0$, respectively. Either one implies that $\partial\alpha/\partial\Delta G^o > 0$. Explicitly, from (6.15),

$$\partial\alpha/\partial\Delta G^o = -1/G_a^o[\partial^2 M/\partial\alpha^2] > 0. \qquad (6.16)$$

Since $\alpha = 1/2$ for $\Delta G^o = 0$, it follows that when $\Delta G^o > 0$, $\alpha < 1/2$ and $G_a$ is only moderately $\Delta G^o$ dependent whereas when $\Delta G^o > 0$, $G_a$ is both larger and more strongly dependent ($\alpha > 1/2$) on $\Delta G^o$.

The Reactivity-Selectivity Principle. The correlation of diminished reactivity (higher $G_a$) with increased selectivity with respect to structural changes (i.e., higher $\alpha = \partial G_a/\partial\Delta G^o$), is sometimes known as the 'reactivity-selectivity principle'. On the other hand, the observed $\Delta G^o$ dependence of $\alpha$ is typically quite moderate, so much so that even the observation that $\alpha$ may depend on $\Delta G^o$ is yet to receive universal acceptance. It follows that the typical intrinsic free energy activation barrier, $G_a^o$, is seldom low and that $M(\alpha)$ has a finite curvature. The dependence of $\alpha$ on $\Delta G^o$ for several values of $G_a^o$ is shown in figure 2.

Example. Figure 3 shows a plot of $G_a$ vs. $\Delta G^o$ for the series of gas phase reactions[28] $X + H_2 \rightarrow XH + H$ (squares). Included in the figure are results[52] (triangles) for the reversed reactions $XH + H \rightarrow X + H_2$ obtained using (6.10). X is a halogen atom. The continous curve is a fit to the data, and $\alpha$ vs. $\Delta G^o$, determined from the continuous curve, is shown as the right hand side panel of the figure. The Legendre transform, $M(\alpha)$ of the continuous curve is

$$M(\alpha) = -[\alpha\log\alpha + (1 - \alpha)\log(1 - \alpha)]/\log 2, \tag{6.17}$$

so that

$$\alpha = 1/[1 + \exp(-\Delta G/G_a^o)], \tag{6.18}$$

is the functional form shown. Many additional examples of the use of the functional form (6.17) to fit experimental data will be found in references 25 and 28. The results shown in figure 3 are however exceptional in the range of $\Delta G^o$ which is included. For most examples, the span in $\Delta G^o/G_a^o$ is much more limited, thereby preventing a critical examination of the $\alpha$-dependence of $M(\alpha)$. The problem is that very general considerations suffice to show that $M(\alpha)$ is symmetric about $\alpha = 1/2$, where it is maximal. While many functions qualify (e.g.,[15-17,27,53,54] $M(\alpha) = 1 - 4(\alpha - 1/2)^2 = 4\alpha(1 - \alpha)$), they all must have the same behavior about $\alpha = 1/2$ and hence can only really differ in their wings, i.e., for $\Delta G^o$ substantially different from RT. Of course, this is precisely the region which is not easily measured in the gas phase and where additional complications enter in solution kinetics.

The selectivity-reactivity principle is very much evident in the left panel of figure 3. It is worthwhile however to draw attention to the scale on the ordinate. It is a logarithmic scale, which tends to gloss over small variations. Isotope effects (i.e., replacing H by D) where the changes in $\Delta G^{o}$ are small cannot be accounted for in this fashion,[25,28] and do require a change in the magnitude of $G_a^{o}$. Similarly, the temperature dependence of the rate constant requires that $G_a^{o}$ does depend on T. In the more general case of reactant state selection, $G_a^{o}$ must be a function of the energy of the reactants. Invoking detailed balance, this implies that rate constants into different products energy states will have different $G_a^{o}$ values and should not be put on a common Brønsted plot. The discussion in section III specifies what needs to be done. *$M(\alpha)$ is the Legendre transform of $G_a$* only with respect to $\Delta G^{o}$. If the role of additional variables is to be explored, one needs to carry out a Legendre transformation with respect to these other variables as well. While the principle is thus clear, considerable work is required in practice before the utility of such an approach is established.

The Activation Energy. A correlation between the activation energy and the standard energy change $\Delta E^{o}$ of the reaction obtains for any Brønsted series. Applying the Gibbs-Helmholtz equation (2.31) to (6.7) and using (6.5) one finds

$$E_a = -T^2 \partial(G_a/T)/\partial T = \alpha \Delta E^{o} + E_a^{o} M(\alpha) \tag{6.19}$$

where

$$E_a^{o} = -T^2 \partial(G_a^{o}/T)/\partial T. \tag{6.20}$$

In particular, it follows that for a Brønsted series, the height of the potential energy barrier to reaction would be correlated with $\Delta E_o^o$ , the change in bond energy. Figure 4 shows such a correlation for the same series shown in figure 3.

Summary. A critical evaluation of the scope and limitation of the functional representation $G_a = \alpha\Delta G^o + G_a^o M(\alpha)$ requires that the rate constants be known for a series of reactions spanning a wide range in $\Delta G^o/RT$. In addition, it would be very useful to know these rates over a wide temperature range and to have some indication of the dependence of the rates on selective reagent excitation (or for different products energy states). The two series which appear as likely candidates for such an evaluation are $X + H_2 \rightarrow XH + H$ and $X + HY \rightarrow XH + Y$, where X and Y are halogen atoms. What is required is more data[44,55] on the temperature dependence of the rate constants. Two other families which will help shed light on $G_a^o$ are[56] $H + XY \rightarrow HX + Y$ and[57] $H + XH \rightarrow HX + H$.

## VII The Interpolation Model

A simplistic model for the form of the free energy of activation is introduced in this section. It offers a complementary point of view to the operational description of section VI. There we took it for granted that a Brønsted series of reactions does exist and concluded that this implies the existence of a function $M(\alpha)$ whose properties were examined. Here we postulate an interpolation formula between the free energies of the reagents and the products and conclude that a Brønsted series can be defined and that $\alpha$ can be given a structural interpretation, as the location of the 'transition state' enroute from reagents to products.[12]

The Progress Variable. Consider n to be a progress variable describing a concerted chemical reaction. n=0 at the reagents side and =1 at the products. It is suggestive to think of n as the order[58] of the new bond. The progress of the concerted reaction is then described as[58,59] the sum of the bond orders of the old and the new bonds is maintained (to be unity) throughout the rearrangement. Such an interpretation is useful but not essential and alternative views of n can be entertained.

The Interpolation Formula

The thermodynamic driving force for the reaction is the free energy difference between products and reagents. The simplest assumption that one can make is that this remains true also during the rearrangement itself; that at any point n enroute from reagents to products the free energy G(n), (measured relative to the reactants)

can be expressed as

$$G(n) + G_r = (1-n)G_r + nG_p. \tag{7.1}$$

Here the subscripts refer to reactants and products respectively, $G(n) = 0$ at $n=0$ and increases linearly with n, $G(n) = n\Delta G$, reading $\Delta G$ at the products, $n=1$, side.

The concept of a potential energy surface provides a theoretical molecular interpretation of the mechanism for the concerted loosening of the old bond and the tightening of the new one.[10,11] It also shows however that repulsion between the non-bonded atoms prevents the reaction coordinate from running entirely down-hill in the exoergic direction. This additional source of inertia, equally present for both the forward and reverse reaction requires that the linear interpolation (7.1) be augmented by a second term, i.e.

$$G(n) = n\Delta G^o + G_a^o M(n). \tag{7.2}$$

Here the n dependence of M(n) is to be such that G(n) does have a maximum at some value of n, say $n=\alpha$. The magnitude of $\alpha$ (which, by construction, is positive and between zero and one) is the solution of

$$[\partial G(n)/\partial n]_{n=\alpha} = 0, \tag{7.3}$$

which, using (7.2), is seen to be equivalent to the previous definition of $M(\alpha)$

$$\Delta G^o/G_a^o = -[\partial M(n)/\partial n]_{n=\alpha}. \tag{7.4}$$

As $\Delta G^o$ varies, so will the magnitude of $\alpha$ which is determined by (7.4). To insure that G(n) is always maximal at $n=\alpha$ we thus need to require that

$$\partial^2 G(n)/\partial n^2 = G_a^o \partial^2 M/\partial n^2 < 0. \tag{7.5}$$

The condition that there is a maximal free energy enroute from reagents to products is this sections way of introducing the inertia of the chemical reaction.

The Hammond and Leffler Postulates. When M(n) is independent of $\Delta G^{o}$, so that M(α) depends on $\Delta G^{o}$ only implicitly (via the dependence of α on $\Delta G^{o}$) it follows from (7.2) and (7.4) that

$$[\partial G(n)/\partial \Delta G^{o}]_{n=\alpha} = \alpha. \qquad (7.6)$$

That the Brønsted coefficient can be equated to the magnitude of the progress variable at the point of maximal free energy is sometimes called the Leffler postulate.[12] It is seen to be a direct consequence of the form (7.2) for G(n) for any convex (cf. (7.5)) function M(n) which is not explicitly a function of $\Delta G^{o}$. These very same conditions also suffice to support the so-called 'Hammond postulate'.[13] Specifically, that for any Brønsted series, the location of the point of maximal free energy shifts towards the products side as $\Delta G^{o}$ increases. As in the operational discussion, (cf. (6.15)), the proof is based on taking the derivative of both sides of (7.4) with respect ΔG, leading to $\partial\alpha/\partial\Delta G^{o} > 0$. The advantage of the model is that it identifies the Brønsted slope α, which satisfies $\partial\alpha/\partial\Delta G^{o}>0$, with the location of the point of maximal free energy. Any irregularities in the monotonic dependence of α on $\Delta G^{o}$ are thus to be taken as evidence that one is not considering reactions of the same series.

The Potential Energy along the Reaction Coordinate. There is one important limitation to the discussion based on (7.2). The operational theory requires that $M(\alpha)$ depends on $\Delta G$ only via its $\alpha$ dependence. This is insured in (7.2) by taking $M(n)$ to be a function only of n, which is independent of $\Delta G$. This assumption is clearly sufficient to prove that $M(\alpha)$ is a function only of $\alpha$ but it is not necessary. Of course, if one is only interested in kinetic behavior, only $M(\alpha)$ is needed, and, for a given series, it is only a function of $\alpha$. If however one wishes to regard the static, zero temperature limit, then $G(n)$ becomes the potential energy as a function of the progress variable for the system (i.e. the potential energy along a reaction coordinate, where the coordinate is n). It then becomes a question of considerable interest whether it is possible to regard $M(n)$ as the same function for the entire series of reactions. An answer in the affirmative would indicate a very useful scaling property for the different potential energy surfaces of the same series. There are at present only very few studies related to this point. Starting with the BEBO representation for the energy along the reaction coordinate, Marcus[17] has shown that the potential energy is not exactly of the form

$$V(n) = n\Delta V + E_a^o M(n) \qquad (7.7)$$

with $M(n)$ independent of the difference, $\Delta V$, in bond energies. However, equation (6.7) is satisfied for the BEBO form of $M(n)$ and, moreover, the $\Delta V$ dependence of $M(n)$ is at best small and can be neglected[18,60] without seriously changing $V(n)$. In addition, it is found[28] that the form (7.7), with $M(n)$ being only n dependent

(as in (6.17)) can represent the energy profile along the reaction coordinate even for highly exoergic processes. It is important to note in this respect that merely examining the prediction of (7.7) for the correlation of the barrier height (i.e. $V(\alpha)$) with $\Delta V$, as in figure 4, will not suffice. The reason being that the result that $M(\alpha)$ is only a function of $\alpha$ defines the Brønsted series. Figure 4 is not a test of the model but only serves to determine the functional dependence of $M(\alpha)$ on $\alpha$. Neither is the proof that the Hammond postulate follows upon taking the derivative of $M(\alpha)$ with respect $\Delta G$ and the same applies to the selectivity reactivity principle. All these results are valid for any Brønsted series of reactions and are consistent with, but do not establish the model.

Energy Consumption and Energy Disposal. The model enables us to correlate the location of the free energy barrier along the reaction coordinate with the systematics of energy requirements and energy disposal in a Brønsted series of reactions. $G_a=G_r-G$ has been interpreted in section II as the excess free energy of the reagents. Of course, $G_a$ need be sufficient to overcome $\Delta G^o$. However, even for an early barrier ($\alpha<1/2$, $\Delta G^o<0$), $G_a^o$ increases monotonically as $\alpha$ increases and reaches $G_a^o$ for a symmetric ($\alpha=1/2$) reaction. The excess free energy in the nascent products is $G_a-\Delta G^o$. It is practically negligible for a late ($\alpha\to1$) barrier (highly endothermic reactions tend to produce nearly equilibrated products). As the barrier shifts to earlier locations, $G_a-\Delta G^o$ increases, being $G_a^o$ for $\Delta G^o=0$ (at $\alpha = 1/2$).

## Figure Legends

1. The free energy of activation vs. $\Delta G^{o}$, the standard free energy change in the reaction for three different Brønsted series (i.e., for three different values of $G_a^o$ where $G_a^o = G_a$ at $\Delta G^o = 0$). Since the Brønsted slope, $\alpha = \partial G_a / \partial \Delta G^o$, is independent of the units of energy, $G_a$ is measured in the same units as $\Delta G^o$ and the units in the graph need not be specified (changing the units will not change the graph but only the numerical values on both scales). The graphs are drawn for the particular choice $M(\alpha) = -[\alpha \ln\alpha + (1 - \alpha)\ln(1 - \alpha)]/\ln 2$ but the general features are valid for any convex function $M(\alpha)$: $G_a$ increases monotonically with $\Delta G^o$ with a rate of increase (the Brønsted slope) which is small for $\Delta G^o << 0$ and increasing as $\Delta G^o$ increases (*cf. figure 2*).

2. The dependence of the Brønsted slope on $\Delta G^o$ for the three series shown in figure 1. As is evident from equation (6.18), $\alpha$ is only a weak function of $\Delta G^o$ for $\Delta G^o$ values in the range $|\Delta G^o| < G_a^o$. Hence, to determine $\alpha$ as a function of $\Delta G$ (and hence $M(\alpha)$) from experimental data, it is necessary to measure the rates both for the very fast ($\Delta G^o < -G_a^o$) or the very slow ($\Delta G^o > G_a^o$) members of the series.

3. A Brønsted plot (left panel) and the results for $\alpha$ vs. $\Delta G^o$ (right panel) for the X + $H_2$ family of reactions (X a halogen atom, T = 500K, $G_a^o$ = 4.08 kcal $mol^{-1}$, adapted from reference 28). The squares are the measured[52] rates for the X + $H_2$ reactions (a slight extrapolation of the Arrhenius plot for F and I was required to provide results at a common value of T for the entire family). The triangles are the rates for XH + H reactions (obtained using detailed

balance). Strictly speaking, M(α) should be determined by performing a Legendre transform of the $G_a$ vs. ΔG plot shown in the left panel. In practice, the functional form (6.17) for M(α) was assumed and only the value of $G_a^o$ was optimized, to yield the continous curve shown. The Brønsted slope (given analytically by (6.18)) is shown in the right panel.

4. Variation of the potential energy barrier height V(α) with the difference $\Delta V = \Delta E_o^o$ in bond energies for the X + $H_2$ series of reactions. (Energies in kcal $mol^{-1}$, adapted from reference 25.) These results can be regarded as the zero temperature limit of figure 3. The continuous curve is $\alpha\Delta V + V_a^o M(\alpha)$ with M(α) and α given by (6.17) and (6.18) respectively ($V_a^o$ = 4.6 kcal $mol^{-1}$). The points shown are literature values[25] for V(α).

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Note added after the conference. It is interesting to note the connection of the present discussion to several other presentations. The representation of the exact rate constant in the form (1.2) has also been discussed by Kuppermann. The concept of importance sampling discussed by Muckerman and Faist is closely related to the discussion in our appendix (although the purpose of the two presentations is somewhat different). The cycle (3.11) has also been considered by Weston and Klein. Finally, Dunning has presented a correlation similar to Figure 4 except that his barrier heights are the results of accurate ab initio computations whereas the points shown in Figure 4 (and in reference 25) are semi-empirical estimates which best account for the experimental results.

Appendix

The appendix provides a derivation of the result $k_r(T) = k_{TST}(T)\kappa(T)$ where $\kappa(T), (\kappa(T) \leq 1)$ is the transmission coefficients along the same lines used to derive the result $k_r(T)=Zp_r(T)$ in section V. As will become clear, the two results indicated are only two special cases of an infinite number of expressions all of which share the common form, that of an upper bound to the reaction rate constant times a reactivity (or a transmission) factor. There are, of course, particular reasons for centering attention on the two special forms (Z is independent of $\Delta G$; $\kappa(t)$ is chosen to be as nearly unity as possible) but, in principle, other choices are possible.

The derivation starts with the general form (cf. (5.8))

$$k(n,T)=\pi B^2 \int_0^\infty dE_t f(E_t) \underline{v}[N_r(n,E_t)/N(n,E_t)] \tag{A.1}$$

With the sampling distribution

$$N(n,E_t) = f(E_t)N(n) \tag{A.2}$$

one obtains

$$k(n,T) = \pi B^2 J_r(n)/N(n) \tag{A.3}$$

where $J_r(n)$,

$$J_r(n) = \int_0^\infty \underline{v} N_r(n,E_t) dE_t \tag{A.4}$$

is the flux of reactive reactants when the reactants are sampled as in (A.2). If $J_b(n)$ is an upper bound to $J_r(n)$,

$$k_r(n,T) = k_b(n,t)[J_r(n)/J_b(n)] \tag{A.5}$$

Here $k_b(n,T)$ is defined as in (A.3) with $J_b(n)$ replacing $J_r(n)$ and the term in the square brackets is, by construction, bounded

by unity. Proceeding to the thermal rate constant

$$k_r(T) = \sum_n [N(n)/N] k_r(n,T)$$
$$= \pi B^2 J_r(T)/N \qquad (A.6)$$
$$= k_b(T)[J_r(T)/J_b(T)]$$

where

$$J_r(T) = \sum_n [N(n)/N] J_r(n,T) \qquad (A.7)$$

and

$$J_b(T) = \sum_n [N(n)/N] J_b(n,T) \geqslant J_r(T) \qquad (A.8)$$

Since, by definition

$$k_b(T) = \pi B^2 J_b(T)/N \qquad (A.9)$$

it follows from (A.8) and (A.6) that

$$k_b(T) = \sum_n [N(n)/N] k_b(n,T). \qquad (A.10)$$

Two particular choices for $J_b(T)$ are (i) the flux of all trajectories that originate from the reactants. Then $k_b(T) = Z$, leading to the results of section V. (ii) the flux of all trajectories that originate from the reactants and that proceed to cross a given surface on route from reagents to products[47-49]. This defines $J_+(T)$ such that $k_+(T)$ is the transition state rate constant[49] and the transmission factor is $J_r(T)/J_+(T)$. If there is a surface of no return than for that surface $J_r(T) = J_+(T)$ and $\kappa(T) = 1$. Otherwise, $\kappa(T) \leqslant 1$. The free energy of activation, $G_+(T)-G(T)$, of the transition state theory rate constant is thus a lower bound to the correct value $G_a(T)$, and equals $G_a(T)$ when $\kappa(T) = 1$. The criterion of locating the surface of no return by maximising $G_+(t)$ has indeed been extensively discussed[48,61-64].

Finally, it is important to note that for a bimolecular reaction

the free energy of activation $G_a$ is independent of the choice of concentration units for the rate constant. In other words, $G_r$ (where $G_a=G_r-G$) is closely related to but not identical to $G^{\ddagger}$ defined by[3,9,15]

$$k_r(T) = (kT/h)\exp(-G^{\ddagger}/RT)/Q \qquad (A.11)$$

where Q is the partition function for the reactants. To establish the relation it is convenient to use the identity[9,65]

$$(kT/h)Q_{rR} = ZQ_{rt} \qquad (A.12)$$

Here $Q_{rt}$ and $Q_{rR}$ are the translational and rotational partition functions for the reactive reactants (where the reduced mass for relative motion is identical for the reactants and reactive reactants). Comparing (A.11) with $k_r(T) = Z\exp(-G_r/RT)/Q$ and using (A.12)

$$G_r + RT\ln Q_{rt} \equiv G_r - G_{rt} \qquad (A.13)$$
$$= G^{\ddagger} + RT\ln Q_{rR} \equiv G^{\ddagger} - G_{rR}$$

or

$$G^{\ddagger} = G_r - G_{rt} + G_{rR} \qquad (A.14)$$

For the reactive reactants the motion is separable into translational and internal contributions. Hence one can factor $Q_r$ as $Q_{rt}Q_{rI}$ where $Q_{rI}$ is the internal partition function. It follows that $G_r-G_{rt}$ (cf. (A.13)) is the internal free energy of the reactive reactants. For the transition state the separable approximation is not necessarily valid[49,66,67]. If it is, one can interpret $G^{\ddagger}-G_{rR}$ as the internal free energy at the transition state. One should note however that one can always[35] express the rate constant as in (A.11), irrespective of the validity of transition state theory, so that

(A.14) can be taken as a definition of $G^{\ddagger}$. The advantage of $G_a=G_r-G$ over $\Delta G^{\ddagger}=G^{\ddagger}-G$ is that the standard state dependence of $G_{rt}$ is exactly cancelled by a similar dependence of the $G_t$ contribution to G, so that $G_a$ is independent of concentration units. Not so for $\Delta G^{\ddagger}$. The elimination of $G_{rt}$ (cf. (A.14)) means that $\Delta G^{\ddagger}$ has the dimensions of[68,69] energy. [dimensionless factor + log (volume)].

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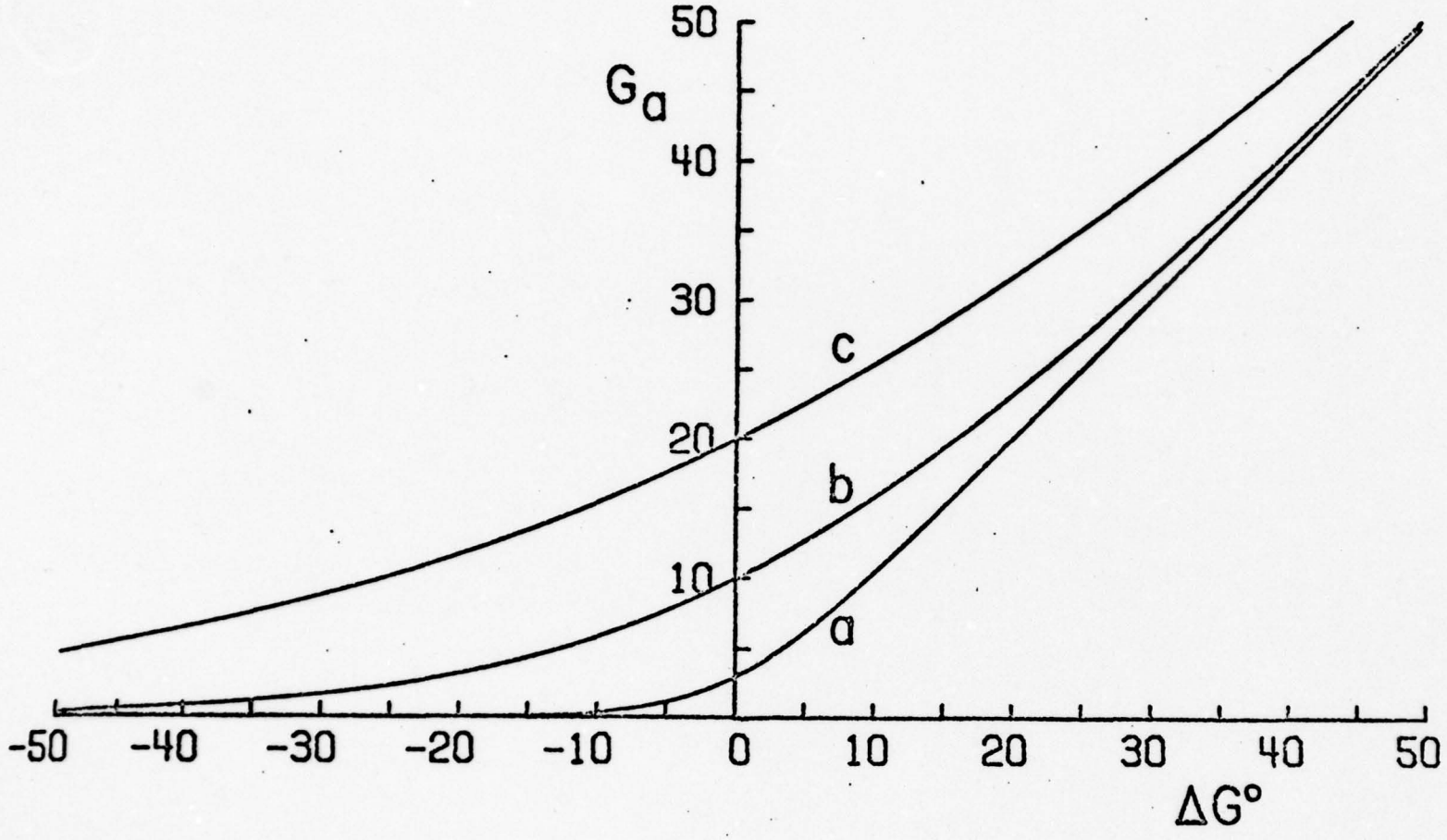



Figure 1

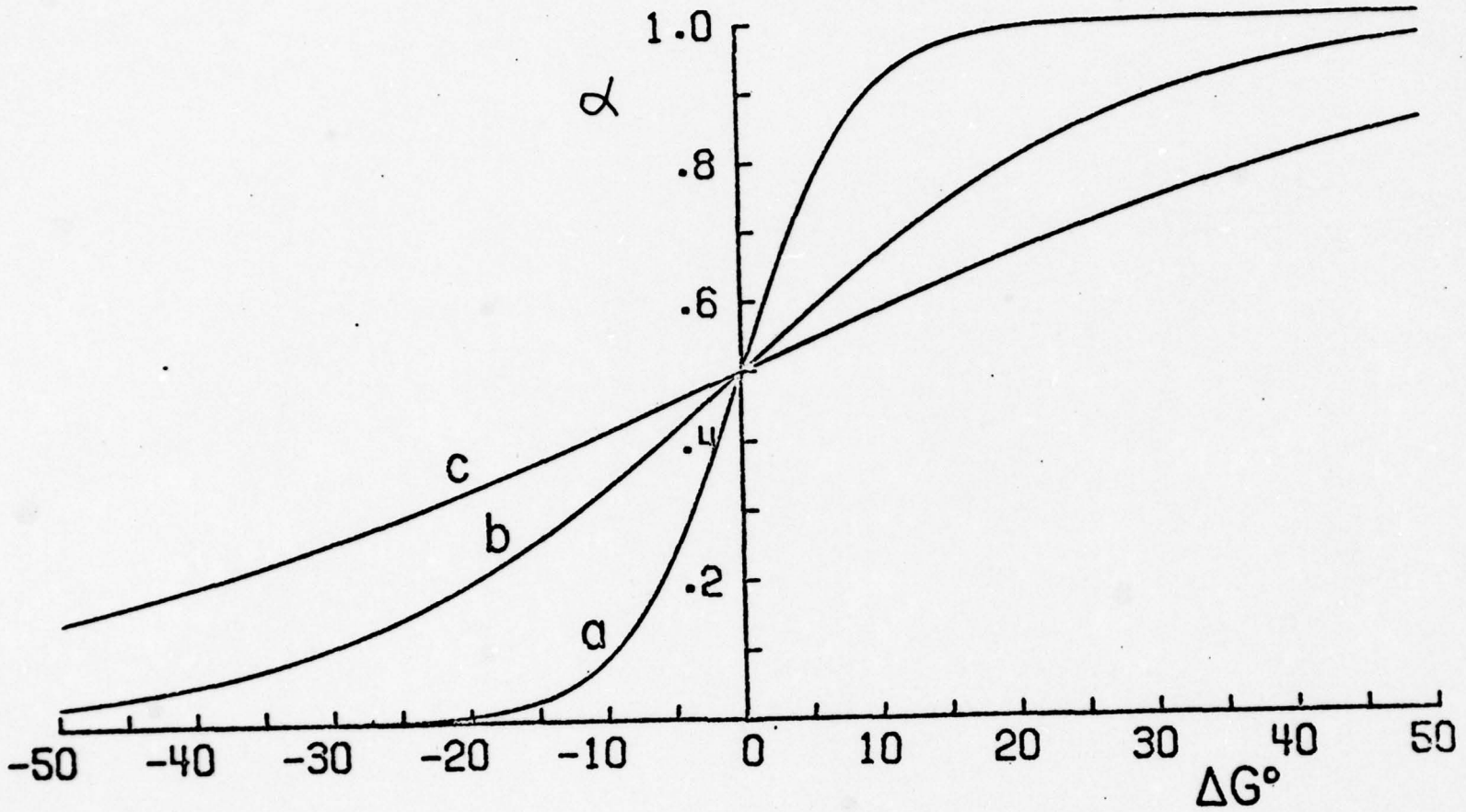



Figure 2

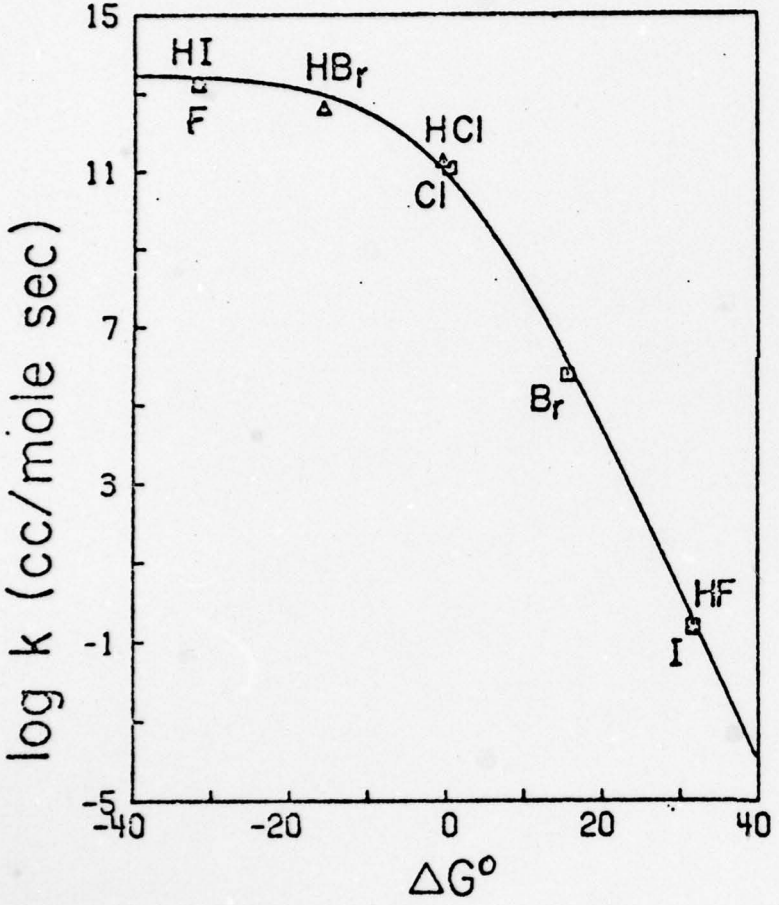



Figure 3

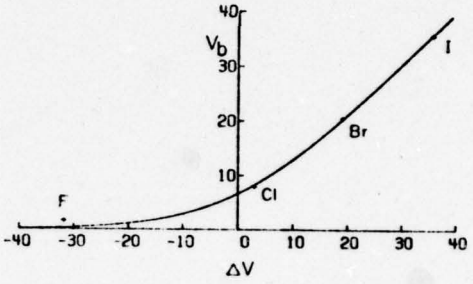



Figure 4

# ENERGY TRANSFER TO A MORSE OSCILLATOR*

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Abstract

The vibrational excitation of an anharmonic (Morse) oscillator in a collinear collision is determined analytically using a dynamical algebra consisting of three operators. Only one parameter is however required to specify the transition probabilities. The dependence of V→T processes on the initial vibrational state is examined. A weak coupling scaling law $P_{n\to n-1} = n[1-(n-1)/2k]P_{1\to 0}$ where k is the number of bound states is derived. At finite coupling strengths the decline of $P_{n\to n-1}/n$ with n is faster than that suggested by the scaling law.

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## I. Introduction

Transition probabilities in molecular collisions often show considerable deviance from that expected if the final phase space is uniformly populated. Surprisal analysis [1] has demonstrated that such deviances can often be characterized as due to simple constraints. Recently, it was shown that such constraints can be identified on the basis of exact dynamical considerations [2,3]. A minimal set of constraints, the 'dynamical algebra', was found sufficient to determine the scattering matrix [3]. Brute force attempts to construct the dynamical algebra for realistic potentials often become cumbersome. The purpose of this letter is to draw attention to a powerful systematic method for the construction of such algebras [4-6] and to demonstrate its application up to and including drawing conclusions of physical interest.

Consider a collinear collision of a particle with a Morse oscillator. In the classical path approximation this collision can be described as the evolution of a Morse oscillator under a time dependent force (which vanishes at $t \to \pm\infty$). We obtain an analytic expression for the transition probabilities and compare with the corresponding results for a harmonic oscillator. The comparison is carried out in terms of the 'reduced anharmonicity' or maximal number of bound states

$$k = (2\mu D_o)^{1/2}/a\hbar$$

which arises as a natural parameter in the formulation of the problem. (Here $D_o$ is the ground state dissociation energy, $\mu$ the oscillator mass and $a$ is the range of the Morse potential [7]). As $k \to \infty$, the results reduce to those [3,8] of the forced harmonic oscillator. The most significant effect for a finite k is the modification of the familiar weak-coupling scaling law of V → T transfer. Here

$$P_{n\to n-1} = n[1-(n-1)/2k]P_{1\to 0}$$

where n is the initial vibrational state.

In addition to obtaining explicit formulas for the quantal probabilities, we also obtain their classical limit and demonstrate that there is a limited band

of final states which are allowed by classical mechanics. The width of the band increases with increasing coupling strength, up to the full width allowed by quantal dynamics.

## II. Scattering Theory

The explicit construction of the scattering matrix in terms of the operators in the dynamical algebra has been presented elsewhere [3]. Here we only state the final result and comment on its adaptation to those dynamical algebras determined by the systematic procedure [4-6]. A detailed presentation of the systematic procedure for the generation of dynamical algebras with special reference to scattering-theoretic applications is in preparation.

For a collision problem in the classical path approximation, consider the following form for the Hamiltonian

$$H = \sum_{n=0} h_n(t) H_n \tag{1}$$

Here the $H_n$'s are operators, with $H_0$ being the Hamiltonian of the unperturbed system. The $h_n(t)$'s are function of time, which, for $n \neq 0$, vanish both before and after the collision. A dynamical algebra is a set of operators $H_n$ which is closed under commutation, [3]

$$[H_n, H_m] = \sum_r C^r_{nm} H_r, \tag{2}$$

and is therefore a Lie algebra [9]. If necessary, the set of operators that appear in H can be augmented by the introduction of additional operators, until the closure condition (2) obtains. For these additional operators, the h(t) coefficients in (1) are to be taken as zero throughout.

Given a dynamical algebra, the evolution operator is of the form (equation (4.3) of ref. 3)

$$U(t,t') = \exp[-(i/\hbar)\sum_n u_n(t,t') H_n] \tag{3}$$

and the scattering matrix is obtained, as usual, by evaluating the matrix elements

of U (in the interaction picture) and taking the limits $t\to\infty$, $t'\to-\infty$). Explicit equations of motion for the coefficients $u_n(t,t')$ have been derived (equation (5.19) of ref. 3).

A systematic procedure for the construction of a Lie algebra for a given Hamiltonian has been presented [4-6]. In particular, it is possible to transform the original Schrodinger operator $K\equiv H-i\partial/\partial t$ to $\tilde{K}$

$$\tilde{K} = DKD^{-1} \tag{4}$$

such that the algebra for K is far simpler. This is particularly so if the spectrum of $H_0$ is known. (See the examples of ref. 5). One can then determine the evolution operator for $\tilde{K}$ and transform back to obtain the evolution operator for K. In practice one is only interested in matrix elements. Specifically, if $\psi_n(t)$ is a solution of the time dependent Schrodinger equation for $H_0$, we need the matrix elements of $U(t,t')$ between the states $\psi_n(t)$ and $\psi_m(t')$. But these are the same as the matrix elements of $\tilde{U}(t,t')$ in the transformed basis $D\psi_n(t)$. (We require that $DH_0D^{-1} = H_0$). Solving the scattering problem for $\tilde{K}$ provides therefore the solution of the scattering problem for K. All that is required for the original problem is to determine the S matrix in the transformed basis.

## III. The Forced Morse Oscillator

The bound state energy levels of the Morse oscillator are [7]

$$E_n = -(a^2\hbar^2/2\mu)(k-n)^2 \tag{5}$$

k is a convenient reduced measure of the anharmonicity and we shall label the bound states by both k and n, although k is fixed for any given physical application. The solution of the time dependent Schrodinger equation for an unperturbed oscillator will thus be written as $\psi_n(t) = \exp(-iE_nt/\hbar)|n,k\rangle$.

The similarity transformation employed here is that of time dilation [5,6] such that

$$D\psi_n(t) = \exp[-i(n-k)t]|n,k\rangle. \tag{6}$$

The transformation linearises the spectrum of $H_0$.

The 'forcing' of the oscillator is described by operators which change its state. In general, the oscillator can also dissociate. To simplify the discussion we shall use an algebra that excludes this possibility and introduce an auxiliary label m such that

$$n = k-|m| \tag{7}$$

so that $m = \pm k$ is the ground state and m takes 2k+1 values from -k to +k. The forcing terms will induce $\Delta m$ transitions,

$$Q_{\pm}|k,m\rangle = c_{\pm}(km)|k,m\pm 1\rangle \tag{8}$$

Here $c_{\pm}(km)$ is a numerical coefficient. To insure that the problem reduces to that of the forced harmonic oscillator and that $Q_+^{\dagger} = Q_-$ we take

$$c_{\pm}(km) = [k(k+1)-m(m\pm 1)]^{1/2} \tag{9}$$

It follows from (8) and (9) that

$$[Q_+,Q_-]|k,m\rangle = 2m|k,m\rangle \tag{10}$$

Hence our algebra also contains the operator $Q_o$,

$$Q_o|k,m\rangle = m|k,m\rangle \tag{11}$$

or

$$[Q_+,Q_-] = 2Q_o. \tag{12}$$

Are there additional operators? By examining the action of $[Q_o,Q_{\pm}]$ on the basis functions one readily verifies that

$$[Q_o,Q_{\pm}] = \pm Q_{\pm} \tag{13}$$

An algebra for the transformed Hamiltonian is given by $\{Q_+,Q_-,Q_o\}$ and is that of SO(3). An explicit coordinate space realization shows that $Q_{\pm}$ are linear combinations of the oscillator coordinate and momenta with coefficients that depend on the coordinate. In the limit $k \to \infty$ they reduce to the algebra of the forced harmonic oscillator [3]. In that limit

$$Q_+ \to (2k)^{1/2} a^{\dagger} \tag{14}$$

where $a^\dagger$ is the harmonic oscillator raising operator and similarly for $Q_-$. Hence

$$[Q_+,Q_-] \to 2k[a^\dagger,a] = 2kI \tag{15}$$

so that $Q_o \to kI$ where I is the identity operator. Now

$$\begin{aligned} &\langle m+1,k|[Q_o,Q_+]|m,k\rangle = c_+(k,m) \\ &2^{1/2}(k)^{3/2}\langle n+1|[I,a^\dagger]|n\rangle = k^{1/2} \end{aligned} \tag{16}$$

or $[I,a^\dagger] = 0$, QED. The algebra we have generated does reduce, as $k \to \infty$ to the dynamical algebra $\{a^\dagger,a,I\}$ of the forced harmonic oscillator.

## IV. Transition Probabilities

The determination of the transition probabilities requires the representation of the evolution operator in the basis $D\psi_n(t)$. The most general form of the scattering operator for the dynamical algebra $\{Q_+,Q_-,Q_o\}$ is

$$S = \exp[i(qQ_+ + q^*Q_- + \delta Q_o)] \tag{17}$$

where, since $(Q_+)^\dagger = Q_-$, S is unitary. One can rewrite S in a product form (cf. equations (4.4) or (5.3) of [3]), and its most general form is ([10], pages 54-55 equation (4.1.8) in particular)

$$S = \exp[i\alpha Q_o]\exp[\beta(Q_+-Q_-)]\exp[i\gamma Q_o] \tag{18}$$

whose representation is [10]

$$\langle m'k|S|mk\rangle = D^{(k)}_{m'm}(\alpha\beta\gamma) = \exp(im'\gamma)d^{(k)}_{m'm}(\beta)\exp(im\alpha) \tag{19}$$

Here the D's are the unitary rotation matrices and the d's are the reduced unitary rotation matrices. The symmetry properties

$$d^{(k)}_{m'm}(\beta) = (-1)^{m'-m}d^{(k)}_{mm'}(\beta) = (-1)^{m'-m}d^{(k)}_{-m'-m}(\beta) \tag{20}$$

will be invoked below.

The transition probabilities among different oscillator states are given by the squares of the S matrix elements

$$\begin{aligned} &P_{n\to n'} = |d^{(k)}_{k-n\ k-n'}(\beta)|^2 = \\ &n!(2k-n)!(n')!(2k-n')!(1+p)^{-2k}\Big|\sum_\nu \frac{(-1)^\nu \rho^{[2\nu-n+n']/2}}{\nu!(\nu-n+n')!(n-\nu)!(2k-n'-\nu)!}\Big|^2 \end{aligned} \tag{21}$$

where $\rho = tn^2(\beta/2)$. They are symmetric (cf.(20)) and normalised.

There is only one group parameter (i.e. $\beta$) that enters the expression for the transition probabilities. In principle, it can be computed from the equations of motion for the group parameters, [3], in terms of the forcing functions $h_{\pm}(t)$ (cf. equation (1)). For the purpose of interpreting the results it is sufficient however to note that to lowest order in the forcing terms (cf. (18))

$$S_{DW} = \exp[i\alpha Q_o][I+\beta(Q_+-Q_-)]\exp[i\gamma Q_o] \tag{22}$$

It follows that in first order the perturbation induces transitions only among adjacent states of the oscillator and that (cf. (16)) the proper coupling parameter is $k\beta^2$.

The final vibrational state distribution is monotonic for transitions out of the ground state (cf. (25) below) but shows a typical quantum interference for $n \neq 0$, as is shown in Figure 1. In the classical limit, these oscillations can be averaged over [11]. The vector model, Figure 2, gives the classical distribution as

$$P_{n\to n'} = (\pi k)^{-1}[(\cos\beta-\cos\nu\cos\nu')^2-\sin^2\nu\sin^2\nu']^{-1/2} \tag{23}$$

where $\cos\nu=1-n/k$. The most probable final states in the classical limit are the two roots of $\beta=\nu'\pm\nu$, which define the end points in the vector model, figure 2.

In the $k \to \infty$ (or harmonic oscillator) limit, we obtain (cf. (14))

$$S = \exp[\alpha(a^+-a)] \tag{24}$$

with $\alpha=(2k)^{1/2}\beta$, which is the previously derived result ([3], equation (3.40)). Explicitly, and using thé $0 \to n$ transitions, we have obtained here (cf. (21))

$$P_{0 \to n} = \binom{2k}{n}[\rho^n/(1+\rho)^{2k}]. \tag{25}$$

Using the Stirling approximation this can be shown to reduce to

$$P_{0\to n} = [g^n/n!]\exp(-g), \quad k \to \infty \tag{26}$$

where $g = 2k\rho(\to 2k\beta^2$ as $\beta\to 0)$, which is the well known result [8] for the forced harmonic oscillator.

Explicit expressions for the mean final quantum number (or higher moments thereof) are readily obtained by differentiating the normalisation condition $\Sigma_n P_{0\to n} = 1$ with respect to $\rho$. One then finds

$$\langle n\rangle \equiv \sum_n nP_{0\to n} = 2k\rho/(1+\rho) \tag{27}$$

$$\langle (n-\langle n\rangle)\rangle^2 = 2k\rho/(1+\rho)^2 \tag{28}$$

In the $k \to \infty$ limit, these reduce to the results (g and g respectively) expected for the harmonic oscillator.

## V. Discussion

The role of the anharmonicity is best demonstrated by comparing the results for the harmonic and the Morse oscillators. Thus the ratio of the 0↦1 transition probabilities (given, using (25) and (26) by $(1+\rho)^{2k}\exp(-g)$), is always below unity. A particularly interesting ratio is that of the de-excitation probabilities $P_{n\to n-1}/P_{1\to 0}$. For the collinearly forced harmonic oscillator and to the lowest order in the coupling strength this ratio is [12]n. For this reason it has become customary [13] to scale the n↦n-1 transition probabilities by n. It is thus of interest to note that the same ratio for the Morse oscillator (in the weak coupling limit) is given by

$$|c_-(km)|^2/|c_-(kk)|^2 = n[1-(n-1)/2k] \tag{29}$$

or $P_{n\to n-1}/n$ is a decreasing function of n. Of course the modified anharmonic scaling, $P_{n\to n-1}/n[1-(n-1)/2k]$ is only valid in the weak coupling limit. Even so it does account for the often observed decline of $P_{n\to n-1}/n$ with n, and does compare favorably with the trends noted, Figure 3, using transition probabilities computed using the full form (21). The corresponding result for excitation is

$$P_{n\to n+1} = (n+1)(1-n/2k)P_{0\to 1} \tag{30}$$

An improved* scaling which remains valid not only as $\rho\to 0$ but as long as $nk\rho<1$ is

*In applying these scaling laws it should however be noted that β (cf. equation 22) was taken to be the same for the 1↔0 and the n↔n±1 transitions. This is correct in the classical path approximation. However, when the relative motion is treated quantum mechanically one expects β to increase somewhat as n increases (reflecting the smaller energy gap for the higher transitions. Approximate procedures for incorporating this aspect in the classical path formulation have been proposed [14]).

$$P_{n\to n-1}=nP_{1\to 0}[(2k-n-1)/2k][1-(2k-n)(n-1)(\rho/2)]^2 \qquad (31)$$

obtained by retaining the first two terms in the sum in (21).

## VI. Summary

In demonstrating the dynamical significance of the information theoretical approach it was argued [3] that one can determine the functional form of the scattering matrix (or of the distribution of final states) without solving the equations of motion. The resulting scattering matrix is then obtained as a function of the group parameters (here $\alpha,\beta$ and $\gamma$, cf. equation (18)). The solution of the equations of motion is required only for the determination of the numerical values of the group parameters [3].

In this paper an explicit construction of the scattering matrix and an examination of the resulting transition probabilities was carried out for a non-trivial collision problem. A key ingredient has been the application of a systematic procedure for the generation of Lie algebras [4-6]. In particular, one can construct dynamical algebras that do allow the Morse oscillator to dissociate or for other types of anharmonic oscillators. A complete account of the scattering theoretic implications of the systematic procedure for the construction of Lie algebras associated with a given Hamiltonian is in preparation.

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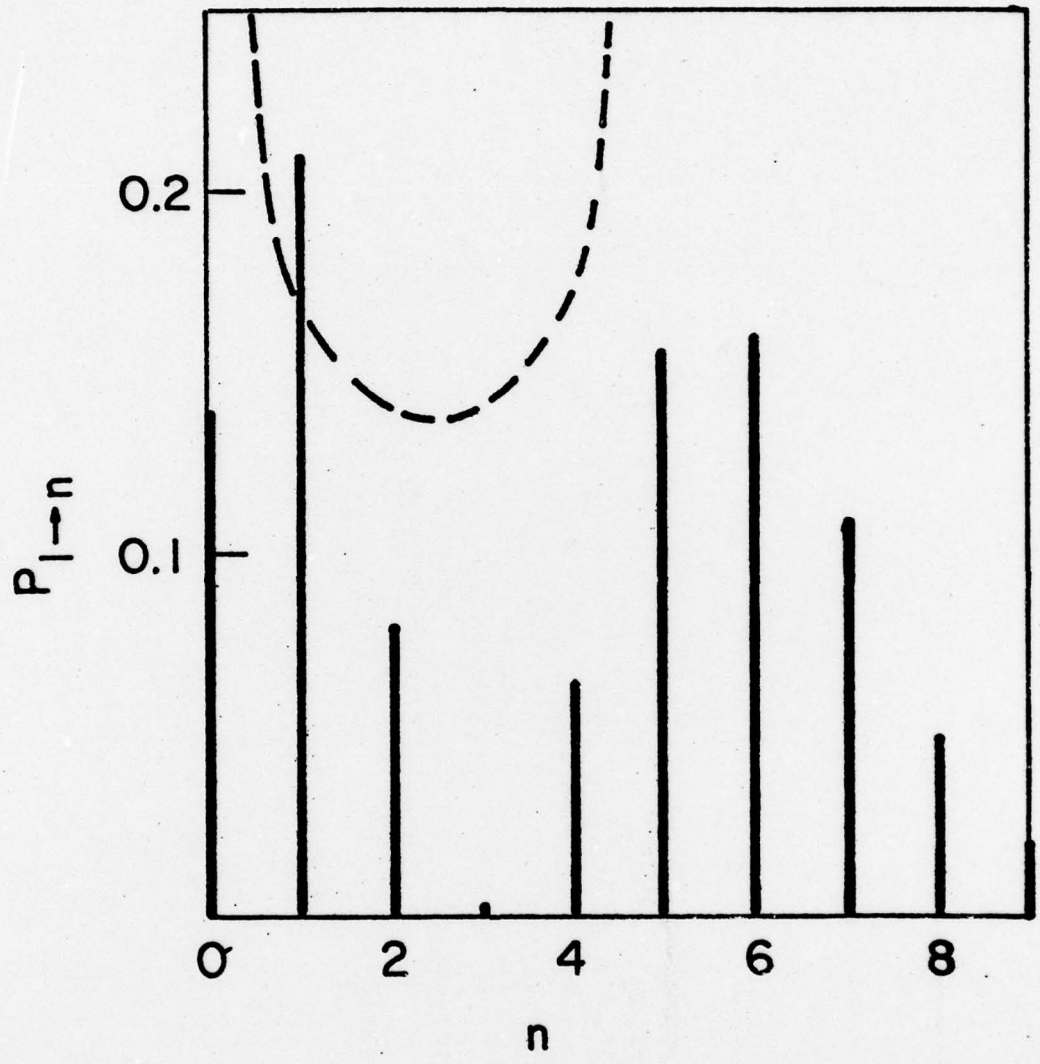
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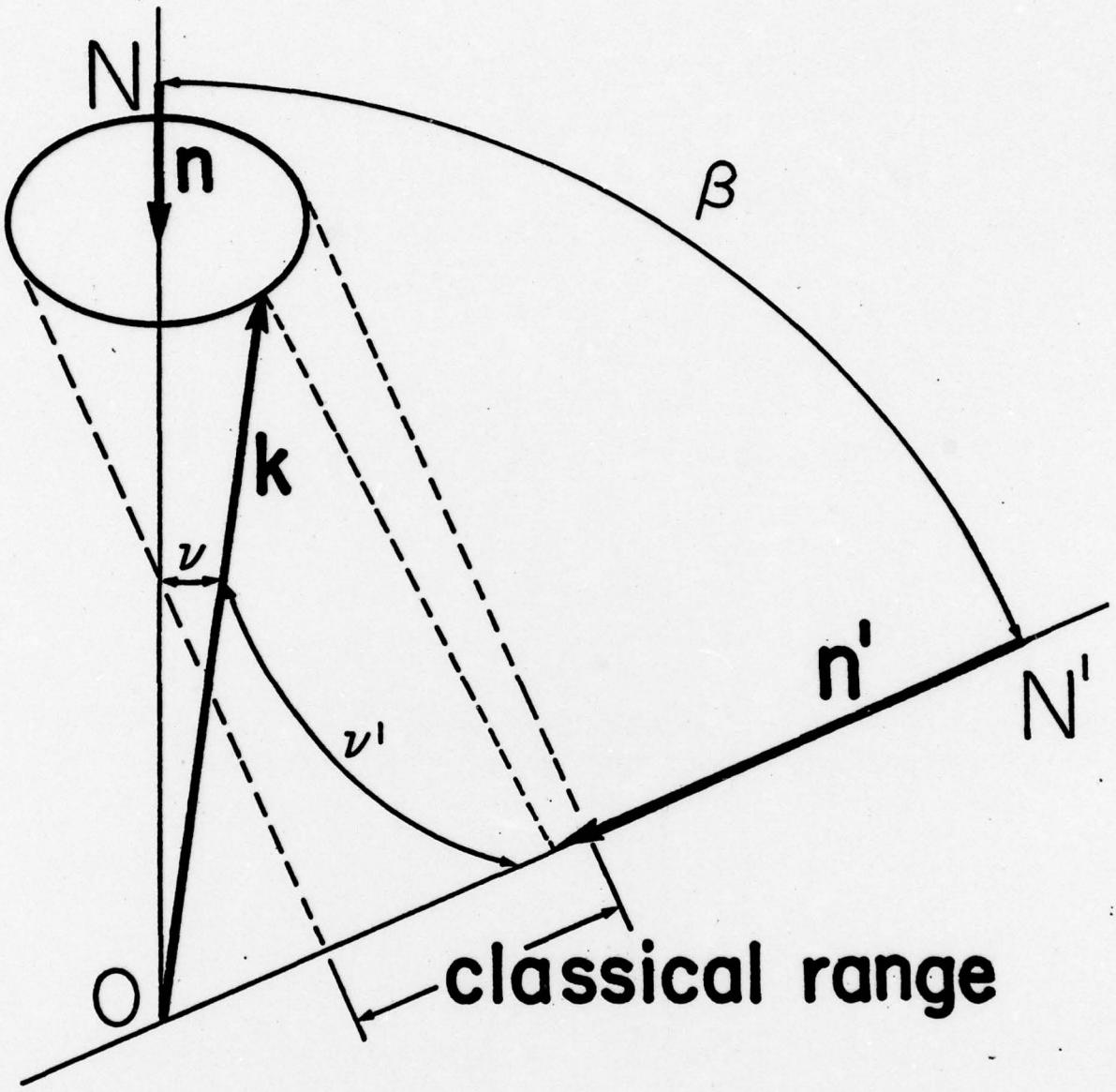
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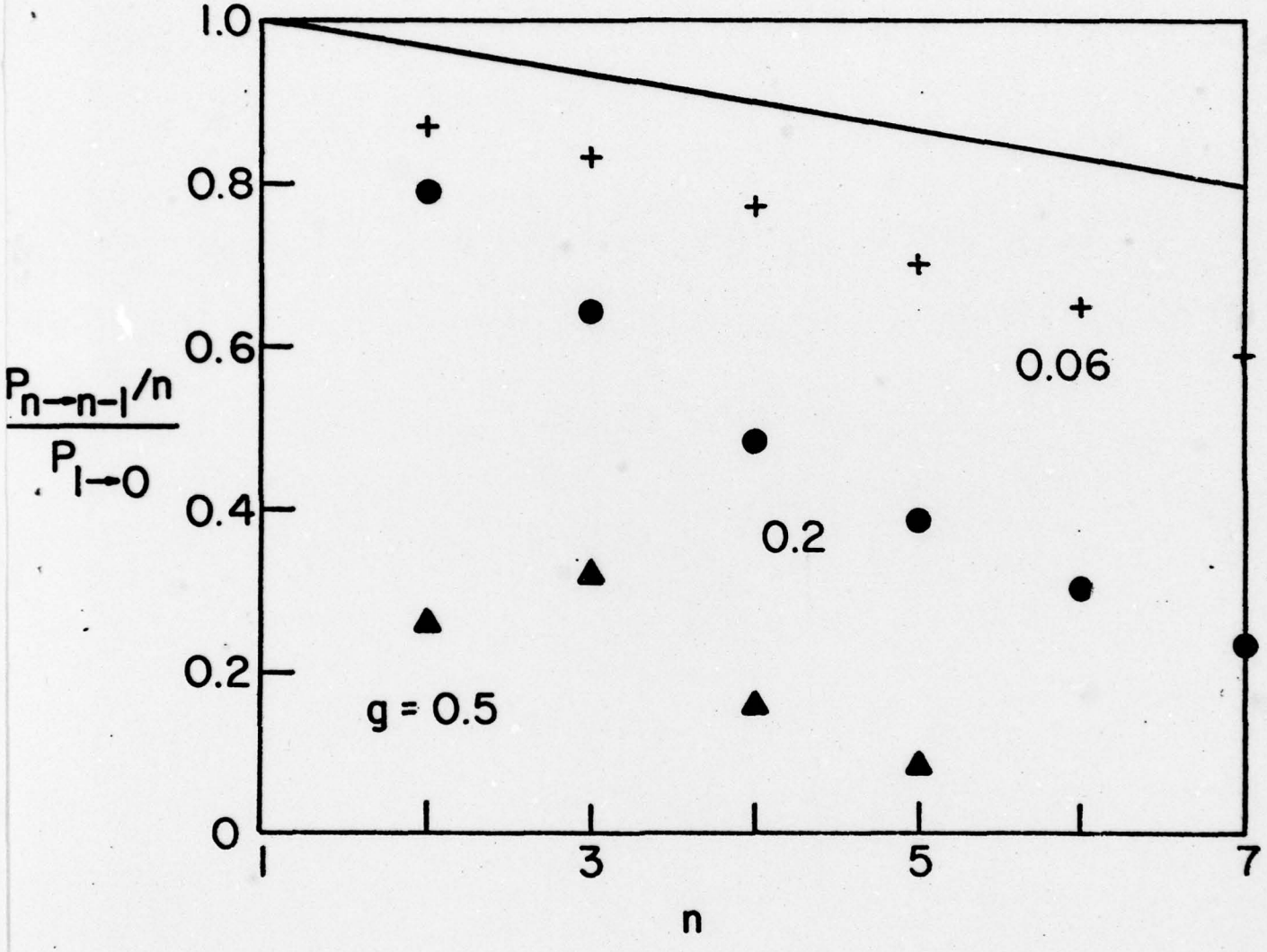
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Figure Legends

1. Transition probabilities for the forced Morse oscillator (at the realistic value k = 15 and intermediate coupling strength $\beta = 36.9°$). The destructive quantal interference for n = 3 is evident. The classical probabilities (equation (23)) are shown for comparison. The states n = 0 and $n \geqslant 5$ are classically forbidden.
2. The vector model for the classical distribution of final vibrational states, based on the classical limit of the d matrices [11]. ON and ON′ are both of length k. The classical $P_{n \to n'}$ distribution is obtained by projecting the tip of the $\underset{\sim}{k}$ vector onto the ON′ axis, while the vector $\underset{\sim}{k}$ spans a circle (perpendicular to the NON′ plane) centered at a distance n from N. The classical turning points, where the probability is maximal, are at $\nu' \pm \nu = \beta$, and the range of n′ values allowed in the classical limit are indicated. The increase of the range of higher vibrational states that are allowed by classical mechanics clearly increases as the strength of the coupling ($\propto \beta$) increases. The transition to the highest bound vibrational state (n′=k) is classically allowed only for $\beta \geqslant 90 - \nu$.
3. The scaling law for n→n-1 transitions for k = 15. In the harmonic oscillator weak coupling limit all the points should be at unity. Solid line: the Morse oscillator weak coupling limit. For finite but weak ($\rho = 1/500$ or g = 0.06 and $\rho = 1/150$ or g = 0.1) couplings, the decline is still monotonic and is well represented by (31). At intermediate coupling ($\rho = 1/60$ or g = 0.5), the behavior is no longer monotonic.


0.2
0.1
$P_{1\to n}$
0
2
4
6
8
n


N
n
β
k
ν
ν'
n'
N'
O
classical range


1.0
0.8
0.6
0.4
0.2
0
$\frac{P_{n\to n-1}/n}{P_{1\to 0}}$
0.06
0.2
g = 0.5
1
3
5
7
n