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QUANTUM MECHANICAL APPROACHES TO CHEMICAL REACTION DYNAMICS

S.D. Schwartz
(Ph.D. Thesis)

March 1984

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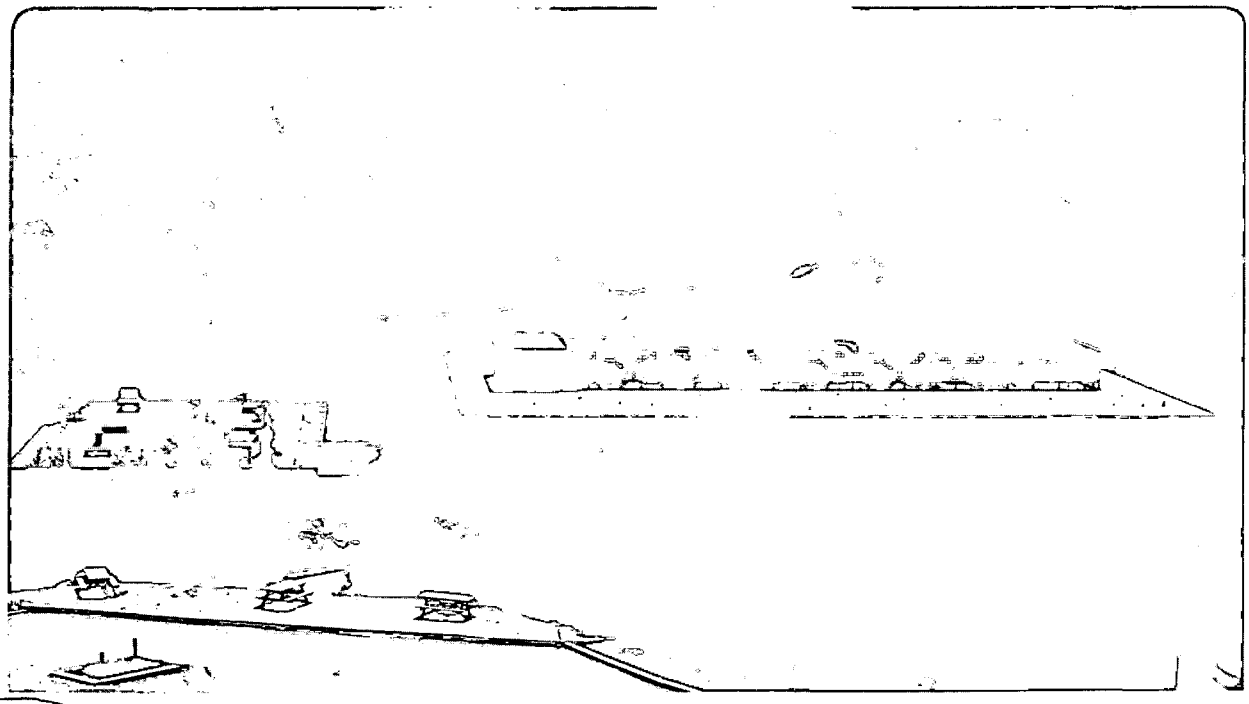

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QUANTUM MECHANICAL APPROACHES TO CHEMICAL REACTION DYNAMICS

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March 1984

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Quantum Mechanical Approaches to Chemical Reaction Dynamics

Steven David Schwartz

ABSTRACT

The physics of chemical processes is most accurately described within a quantum mechanical framework; and so three quantum mechanical approaches are proposed and applied to problems of chemical reaction dynamics.

We first investigate a method to treat the dynamics of large chemical reactions using the Distorted Wave Born Approximation. We employ the concept of separation of the entire dynamical problem into a system and a bath of modes which are weakly coupled to the system. It is felt that because chemical reactions are usually site specific, hence highly localized phenomena, this method of attack will prove useful. This use of scattering perturbation theory differs from more common approaches; in that it couples degrees of freedom rather than quantum states. The theory is applied to the reaction $H+H_2$, and even in this very small reaction, highly accurate results obtain.

The second theoretical approach we employ is a casting of exact quantum mechanical rate constants in terms of various statistical mechanical correlation functions. The correlation functions depend on evaluation of the Feynman propagator for the system at complex values of the time. Methods are developed to apply these formulae to specific cases. Propagators are evaluated along the real line, and

then numerically continued into the complex plane to yield the desired result.

The final chapter deals with a model for the interaction of oscillators with reaction paths through the variation of frequency in the oscillator as it proceeds along the reaction path. The model forms an analogy to simple quantum field theory. In application to an elementary bound state test problem highly accurate results are produced.

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Table of Contents

I. Introduction 1

II. Weakly and Strongly Coupled Degrees of Freedom in Scattering Theory

a - Introduction to the Distorted Wave Technique 6

b - The System-Bath Decomposition 11

c - Perturbative Treatment of the System-Bath Coupling 15

d - Application to $H+H_2$ - Preliminaries 24

e - A Bath of Bends 26

f - Results 33

III. Quantum Mechanical Rate Constants

a - Introduction 36

b - Definition of a Quantum Mechanical Rate Constant 38

c - Alternate Forms of the Rate Constant 46

d - Applications -- One Dimensional Problems 51

IV. Frequency Variation Along a Reaction Path

a - Introduction 67

b - Theoretical Method 68

c - Application 71

d - Remarks 74

V. Conclusion 76

References 77

Figure Captions 79

Figures 80

I - INTRODUCTION

Theoretical chemical dynamics is a subject which has received serious attention for over twenty years. It is, of course, not possible to date any field of inquiry, but one might place the start of serious computational work with the Distorted Wave Born study of Mortensen and Pitzer[1] in 1962. This was one of the first attempts to use ab initio methods to predict detailed quantum mechanical scattering data for a chemical reaction. The notion that quantum mechanics could be productively used to predict chemistry accurately was not at all new, but this use must have seemed quite remarkable. Previously quantum theory had been used for less exact, but more physically motivated, approximate explanations of chemical properties. Pauling and co-workers[2] had used quantum mechanical descriptions of the chemical bond to help elucidate many phenomena in chemical physics, but these theories were approximate, non-computational applications concerned primarily with static properties rather than dynamic ones.

With the computation of the $H+H_2$ cross sections by Mortensen and Pitzer the floodgates were opened. A vast refinement of the Distorted Wave technique was found in the work of Karplus and Tang[3] in 1965. Miller[4] followed with another advance in the method. Coeval with these developments in quantum mechanics, other methods were being developed. Karplus, Porter, and Sharma[5] set out the detailed method for using purely classical theory to determine reaction data. The

original beautiful work of Ford and Wheeler[6] on semiclassical elastic scattering was extended to inelastic and reactive scattering by Pechukas[7], Miller[8], and Marcus[9].

After the passage of more than twenty years, we might chart the progress of computational approaches to chemical dynamics. We would unfortunately be very disappointed with the results. As of now, the only fully converged, fully three dimensional reaction for which quantum mechanical scattering data has been obtained is our old friend $H+H_2$[10]. This was completed with only an almost super-human expenditure of human and computer time. If we proceed to the next most elementary step, and study the reaction H_2+D in three dimensions, the required effort is increased by roughly a factor of twelve[11]. Non-converged results for the three dimensional reaction H_2+F have been computed[12], but this is clearly as far as we are going to go in the near future. It seems fairly clear that large molecules, such as small hydrocarbons, will never be amenable to the methods currently employed for computation.

The other methods already mentioned for studying chemical reactions have also enjoyed a lot of attention. Classical trajectory studies of the type pioneered by Karplus and co-workers[5] have become so popular that a virtual industry has grown up around them. These approaches are inexpensive (or rather they don't consume the massive amounts of time and money necessary for quantum mechanical studies), and they provide a pleasing physical picture. One can actually follow a classical trajectory, and watch how atoms and molecules interact on a Born-Oppenheimer potential energy surface. It is often easier to

picture physical processes in classical rather than quantum mechanics, and so the great popularity of this approach is easy to comprehend. The difficulty with this approach is that it doesn't always work. Firstly, the world of chemistry, contrary to a lot of popular publicity, is quantum mechanical. Secondly, and more importantly, though these methods sometimes do work, we can't predict with any certainty when this will occur. The classic example is found in the collinear study of the H_2+F reaction[13]. If one integrates the classical equations of motion from the reactant valley on the Muckerman 5 potential energy surface and then performs quasi-classical boxing in the product region, one obtains vastly different results than that obtained by the reverse procedure, that is if one integrates from the products to the reactants and does the boxing in the reactant region. It would seem that this discrepancy is due to the fact that by boxing one treats the region of phase-space differently than by Monte Carlo sampling. It turns out in the H_2+F case, proceeding from products to reactants gives answers most closely approximating the true quantum calculation. The difficulty is that one might never have guessed, a priori, that this would be the case. (As a matter of fact, this backward integration seems to violate our esthetic sense of the way the world should work.) In any problem in physical chemistry there's nothing wrong with being wrong, but it is crucial to know why and when you are likely to be wrong. In this H_2+F study this was obviously not the case, and one had to know the answer to get the answer. The final computational method which has received a great deal of attention is of course semi-classical

mechanics. It was hoped that this would combine the clearness of interpretation of classical theory with the formal beauty and accuracy of exact quantum theory. Unfortunately, though the theory is certainly beautiful and can be very accurate[14], it has proved extraordinarily difficult to implement. Technical limitations we shall not discuss make application of the full theory about as difficult a task as application of exact quantum mechanics.

In light of the great difficulties encountered by accurate quantum calculations and the inaccuracies in the classical approximation, this thesis will address the problem of chemical dynamics using approximate and exact theories of rigorous quantum mechanics. Our general philosophy is that it is possibly better to make approximations to an exact dynamic framework than to use a starting point which is at best approximate. Of course, this is a matter of taste, and classical and semi-classical mechanics maintain their use as important methods of inquiry. It is also possible that methods for doing exact scattering calculations quantum mechanically may undergo revolutionary developments which would allow more complicated physical systems to be treated exactly.

In section II we examine a new type of distorted wave theory for scattering. This section utilizes a separation of the problem into weakly and strongly coupled degrees of freedom, rather than the more standard weak coupling assumed between various quantum states. Application to three dimensional $H+H_2$ is made to demonstrate the feasibility of this technique for actual systems.

Section III contains a new approach to the determination of

exact quantum mechanical Boltzmann rate constants. Formal manipulations will be presented which allow the expression of the rate constant of a bimolecular reaction in terms of various statistical correlation functions. Methods of application of these formal developments will be presented.

Section IV will suggest a new way to look at the problem of frequency variation along a reaction path. Analogies will be made to elementary problems in quantum field theory which will help to explain observed effects. Finally Section V will briefly conclude.

II - Weakly and Strongly Coupled Degrees of Freedom in Scattering Theory

a - Introduction to the Distorted Wave Technique

Perturbation theory is certainly the most ubiquitous method of doing physics. The basic idea is straightforward and a common one to all physicists. A simple problem is solved exactly, and small deviations from the simple problem are dealt with only approximately. The standard method in a bound state problem is to develop the wavefunction in a Taylor series and associate a similar series for the energy. Terms in the two series are matched and kept to a given order. An exactly analogous approach is used in scattering theory. Here it is simplest to work with operator calculus on the Green or scattering operator. These derivations are standard, but for completeness we will include a brief sketch of the ideas. The derivations will closely follow those in the excellent text by Taylor[15]. Consider a general system given by:

$$H^o = P^2/2m = T \quad ; \quad H = T+V. \qquad \text{IIa-1}$$

Let us define:

$$G^o(z) = (z-H^o)^{-1} \; ; \quad G(z) = (z-H)^{-1}. \qquad \text{IIa-2}$$

These are the Green or resolvent operators, in which z is any complex

number for which the operator inverse exists. To study these operators, let us first assume that the Hamiltonian admits bound states but no scattering eigenfunctions. In other words, there exists some basis in Hilbert space such that:

$$H|n\rangle = E_n|n\rangle \qquad \text{IIa-3}$$

and we may resolve the identity as the infinite but countable sum

$$1 = \sum_n |n\rangle\langle n|. \qquad \text{IIa-4}$$

Thus

$$G(z) = (z-H)^{-1}\Sigma_n|n\rangle\langle n| = \Sigma_n|n\rangle\langle n|/(z-E_n). \qquad \text{IIa-5}$$

This is a perfectly well behaved function as long as z does not equal an eigenvalue in the spectrum of H. The matrix element of the Green operator will have simple poles at the eigenvalues. For a problem which also admits scattering solutions, that is eigenfunctions with positive energy, then there is a branch cut on the positive real energy axis.

The final fact we need is the operator identity

$$A^{-1} = B^{-1} + B^{-1}(B-A)A^{-1}. \qquad \text{IIa-6}$$

From this simple identity (which is trivially proved by multiplying from the left by B and the right by A) a good deal of the fuel for formal scattering theory is provided. We may, for example let A=z-H

and $B=z-H^o$ to obtain:

$$G(z) = G^o(z) + G^o(z)VG(z). \qquad \text{IIa-7}$$

This is the famous Lippmann-Schwinger equation[16], which was obtained by Lippmann and Schwinger only through a good deal more work. Let us consider an operator defined by the equation

$$T(z)=V+VG^o(z)T(z). \qquad \text{IIa-8}$$

This definition seems a bit arbitrary, but it's not hard to show that this operator is directly related to the standard t matrix:

$$t_{n'\leftarrow n}=\lim_{\varepsilon\downarrow 0} \; T(E_n+i\varepsilon)_{n'\leftarrow n} \qquad \text{IIa-9}$$

Substitution of IIa-7 in IIa-8 yields the iterative equation:

$$T = V + VG^oV + VG^oVG^oV +\ldots. \qquad \text{IIa-10}$$

This is the famous Born series, and it forms the basis for perturbation theory in scattering dynamics. Truncation of the series at various powers of V results in different orders of approximation to T. If V is everywhere small, it seems intuitive that this series will converge and converge quickly. If V is not small, it may converge slowly or not at all. It does turn out that these common-sense ideas are true, and the reader is referred to a beautiful, but

difficult, analysis of Weinberg[17].

Since this series will not converge for large potentials at a rate fast enough to make it useful, we are forced to take our analysis a bit further. It was mentioned before that in standard bound state perturbation theory a reference potential is taken, and one studies variations about it. In order to obtain the Born series, the reference potential taken was V=0. We see then that the Born series will work only if the particle is almost a free particle (or if we are incredibly lucky). Now let $V=V^o+V^1$, where we assume we can solve the scattering problem associated with the potential V^o exactly. A similar analysis to that for the free particle reference provides to first order what is known as the Distorted Wave Born Approximation:

$$t_{n'\leftarrow n} \cong t^o{}_{n'\leftarrow n} + \langle \chi_{n'}{}^- | V^1 | \chi_n{}^+ \rangle. \qquad \text{IIa-11}$$

Here $t^o{}_{n'\leftarrow n}$ is just the transition matrix obtained from the potential V^o. $\chi_{n'}{}^-$ is a scattering state, also generated by the potential V^o, subjected to incoming wave boundary conditions. $\chi_n{}^+$ is a scattering state subject to outgoing boundary conditions. (This is a confusing proposition: we note that the final state is an incoming wave and the initial state is an outgoing wave. A number of justifications have been proposed[18], but we feel this is just one of the perversities of mathematical physics, and justifications simply cloud the issue.)

This Distorted Wave Born Approximation thus greatly extends the applicability of perturbation theory. The problem now boils down to

finding a potential for which exact solutions can be found, and which is not too far different from the actual potential. In problems of chemical interest, chiefly chemical reactions occuring on one Born -Oppenheimer potential energy surface, it is hard to imagine a piece of the potential which we can solve, and another piece which is a perturbation. The standard method is that of Miller[4] which allows one to obtain distorted waves χ^- and χ^+, by any means available, and then to express the transition matrix as:

$$t^1_{n'\leftarrow n} \cong \langle \chi_{n'}^- | H-E | \chi_n^+ \rangle \qquad \text{IIa-12}$$

where H is the total Hamiltonian. The accuracy of our approximation will depend on the accuracy of our distorted waves. Clearly if we are insightful enough to guess the exact answers, χ^+ and χ^- will be eigenfunctions of H (at energy E) and $t^1=0$. This simply means that all the information is contained in the zeroth order operator. The easiest guesses to make are simple elastic scattering functions. It seems intuitive that this will not give a spectacular answer (and it often dosen't). Hubbard and co-workers[19] have recently suggested use of inelastic non-reactive wavefunctions as the distorted waves. In this work we take a totally different approach - we return to the original conception of actually dividing the potential. In the next section we outline a physically obvious way of doing this.

b - The System-Bath Decomposition

The goal of our work is now to find a description of a chemical reaction which will facilitate a decision on the division of the potential. The reaction path Hamiltonian of Miller, Handy, and Adams[20] is just such a description. This Hamiltonian has been described at great length elsewhere[21], so we here sketch only a few salient features. A reaction path is identified as the gradient path on the potential energy hypersurface. All modes orthogonal to this reaction path are treated harmonically, but coupling between the various modes and between the harmonic modes and the reaction path are explicitly described. The idea we pursue here is that only a few of these modes will be strongly coupled to the reaction path. This is not unreasonable when we realize that in a large system, atoms far from the reaction center probably won't influence the outcome of a reaction too greatly. The other modes will be treated as a bath in which a system operates. If the bath has a weak enough coupling to the system, we may accurately treat it as a perturbation. This system-bath decomposition is exactly the type of division we decided was needed in the last section. The classical reaction path Hamiltonian for total angular momentum J=0 is given by

$$H(P_s,s,\{P_k,Q_k\}) = \tfrac{1}{2}\,[P_s-\textstyle\sum_{k,k'}{}^{F} Q_k P_{k'} B_{k,k'}(s)]^2/[1+\sum^{F}_{k=2} Q_k B_{k,1}(s)]^2 + V_o(s) + \sum^{F}_{k=2}(\tfrac{1}{2}P_k{}^2 + \tfrac{1}{2}\omega_k(s)^2 Q_k{}^2). \qquad \text{IIb-1}$$

Here (s,P_s) is the reaction coordinate and its conjugate momentum, and $\{Q_k,P_k\}$ is the set of mutually orthogonal coordinates and momenta for the normal mode vibrations in the hyperplane normal to the

reaction path. The set $\{B_{k,1}(s)\}$ are the curvature coupling elements which give the mutual interaction of the reaction path with normal mode k. The set $\{B_{k,k'}(s)\}$ couple normal modes amoung themselves. $V_o(s)$ is the potential energy along the reaction path, and $\{\omega_k(s)\}$ are the frequencies of the normal modes. It is crucial to note that both the couplings and the frequencies are functions of s, the distance along the reaction path. (It is of course reasonable that in the strong interaction region these quantities will be very different than in the entrance and exit valleys.)

In order to implement the system-bath approximation[22], let us assume that vibrational modes k=2,3,···,f are strongly coupled to each other and to the reaction coordinate - these are the modes which will comprise the system. The remaining modes k=f+1,···,F form the bath. We now take the classical Hamiltonian function and expand it to first order with respect to the bath couplings. We have:

$$H_o = H_{sys} + H_{bath} \qquad \text{IIb-2a}$$

$$H_{sys} = \tfrac{1}{2}\,[P_s - \textstyle\sum^f_{k,k'=2} Q_k P_{k'} B_{kk'}(s)]^2/[1+\textstyle\sum^f_{k=2} Q_k B_{k,1}(s)]^2 + V_o(s) +$$

$$+ \textstyle\sum^f_{k=2} (\tfrac{1}{2} P_k^2 + \tfrac{1}{2}\omega_k^2(s) Q_k^2)$$

$$H_{bath} = \textstyle\sum^F_{k=f+1} (\tfrac{1}{2} P_k^2 + \tfrac{1}{2}\omega_k^2(s) Q_k^2). \qquad \text{IIb-2b}$$

The perturbation is given by:

$$H_1 = [P_s - \textstyle\sum^f_{k,k'=2} Q_k P_{k'} B_{kk'}(s)]^2/[1+\textstyle\sum^f_{k=2} Q_k B_{k,1}(s)]^2 \times$$

$$\sum^{f}_{k=2}\sum^{F}_{k'=f+1} (Q_k P_{k'} - Q_{k'} P_k) B_{kk'}(s) -$$

$$-[P_s - \sum^{f}_{k,k'=2} Q_k P_{k'} B_{kk'}(s)]^2 / [1+\sum^{f}_{k=2} Q_k B_{k,1}(s)]^3 \times$$

$$\sum^{F}_{k=f+1} Q_k B_{k1}(s). \qquad \text{IIb-2c}$$

In action angle variables, another term in the perturbation is found:

$$H_1' = -[P_s - \sum^{f}_{k,k'=2} Q_k P_{k'} B_{kk'}(s)] / [1+\sum^{f}_{k=2} Q_k B_{k,1}(s)]^2 \times$$

$$\sum^{F}_{k=f+1} Q_k B_{kk}(s) \qquad \text{IIb-2d}$$

where $B_{kk}(s) = -\frac{1}{2}\,\omega'_k(s)/\omega_k(s)$ IIb-2e

It is easy to see that the first term in IIb-2c gives the perturbation induced by the coupling of bath modes to system vibrational modes, while the second term gives the coupling of bath modes to the reaction coordinate. The last term in the perturbation is a bit more subtle, and it arises from the indirect coupling of the bath to the reaction coordinate through variation in the frequency. This term will receive a great deal of attention later when we discuss the application of the model to the three dimensional $H+H_2$ system. Now we have the classical Hamiltonian divided into a zeroth order part and a perturbation. As yet, however, we have no idea how to make use of this classical Hamiltonian function. The terms in

equation IIb-2c can be converted directly into a quantum mechanical Hamiltonian operator through the use of Podolsky's formula[23] for the generation of a Hamiltonian operator. Application of this method yields a symmetrized version which we might have guessed. The terms given by the quantum version of IIb-2c will not be crucial in what follows, so we will not list the operator which is obtained. The term given by equation IIb-2d is more complicated. As was stated, to find it one has to convert the Hamiltonian function to action angle variables. This is a mixed representation, or one in which the new coordinates are functions of both cartesian coordinates and momenta[24]. It is not possible in this case then to transform IIb-2d directly to a quantum mechanical operator. We will see when we investigate the $H+H_2$ case that a term such as this will arise naturally from a purely quantum mechanical point of view.

A few comments may now be made about our approximate Hamiltonian. By assumption, our zeroth order Hamiltonian is vibrationally adiabatic in the bath coordinates. To zeroth order, we assume no interaction between the system and the bath. This is another way of saying that to zeroth order whatever quantum state the bath starts in, it will end up in. This is not an unreasonable proposition, because to zeroth order the bath is uncoupled (except by energy conservation) from the system, and so from the reaction path. This is the approximation behind the rotating collinear model of Child[25] and Wyatt[26]; and Walker and co-workers[27] have used it recently to construct cross sections for a number of reactions. One assumes that the bath simply subtracts energy from the system. It is also

important to note again that this is a total J=0 Hamiltonian. It is our feeling that except for reactions in which it is clear that rotations are a major component of the reaction path, total angular momentum should be coupled weakly enough to be included in the bath. (A possible exception would be something like the reaction HCN → HNC where the reaction path is basically a rotation[28].) This idea will be made more explicit in the next section.

c - Perturbative Treatment of the System-Bath Coupling

We now use perturbation theory to obtain quantum mechanical expressions for the effect of the bath on a scattering event. The reaction path Hamiltonian is a coordinate system not quite like those normally used in the discussion of formal scattering theory. Normally we think in terms of radial coordinates, and so scattering wavefunctions depend on a coordinate r which takes the range $[0,\infty)$. The reaction coordinate s, on the other hand, takes the range $(-\infty,\infty)$. Instead of the scattering matrix and the transition matrix, we will have to speak about transmission and reflection matrices. In this section we will derive all the relations necessary for working with these quantities. It is unfortunate that both the transition and transmission matrices are denoted by a small t. In order to avoid confusion, we now state that t will refer solely to the transmission matrix for the remainder of this chapter.

The perturbation method assumes a series expansion for the transmission operator:

$$t_{n',n}(E) = t^{o}_{n',n}(E) + t^{1}_{n',n}(E) + \ldots \qquad \text{IIc-1}$$

Here the symbol n is meant to refer to some composite quantum number which describes all degrees of freedom. The zeroth order term is the transmission amplitude which results from H_o (equation IIb-2b). In order to help clarify what follows, we will work with formulae in which the system explicitly contains two degrees of freedom. (That is one orthogonal mode coupled to the reaction path.) The system is thus mathematically equivalent to a collinear atom - diatom reaction. The zeroth order transmission amplitude must be diagonal in bath quantum states, so the transmission amplitude must take the form:

$$t^{o}_{n',n}(E) = t_{n_2',n_2}\,\delta_{n_3',n_3}\,\delta_{n_4',n_4}\cdots\delta_{n_F',n_F}. \qquad \text{IIc-2}$$

This reduced amplitude is the result of a collinear-like scattering calculation with the vibrationally adiabatic bath serving only to modify the effective potential along the reaction coordinate:

$$V_{eff}(s) = V_o(s) + \sum^{F}_{k=3} (n_k + 1/2)\omega_k(s) \qquad \text{IIc-3}$$

We wish to make clear that because this is mathematically a collinear problem, it is in no way implied that the system is physically a collinear one. It will be physically collinear only if the reaction path is collinear. (That is if the preferred orientation of approach is the collinear one.) If this is not the case the system will

reflect the dominant mode of approach on the potential energy hypersurface. This is one of the major advantages to our system bath approach. The theory automatically modifies itself for each physical situation, and moreover, the inclusion of only strongly coupled modes automatically supports the use of perturbation theory. This is to be compared to methods in which one hopes that reaction is a small enough effect to be treated as a perturbation.

Another immediate advantage is that for a truly large system, that is greater than four or five atoms, as long as most of the modes are weakly coupled, the zeroth order system is relatively easy to solve. It is not unreasonable that most of the modes will be weakly coupled because chemical reactions tend to be site specific and so are local phenomena. For a six atom system, current technology would be rather hard pressed to provide one with inelastic wavefunctions for a more standard distorted wave calculation. (It should now be mentioned that the statement that as the system gets larger the computation probably won't get too much harder refers only to the scattering calculation. It is of course true that the quantum chemistry necessary for computation of the reaction path data becomes much more difficult as the system grows. We always assume that sympathetic quantum chemists can be found to implement this part of the calculation.) We can also note at this point how overall non-zero angular momentum would be included in the bath. We simply would modify the effective potential to read

$$V_{eff}(s) = V_o(s) + \sum_{k=3}^{F} (n_k + 1/2)\omega_k(s) + B(s)J(J+1). \quad \text{IIc-4}$$

B(s) is the rotation constant for the entire reacting system, and it is of course a function of position along the reaction path. (In order to implement this, one would have to fix all harmonic modes at their equilibrium positions for the calculation of the moment of inertia tensor necessary for B(s).) One final comment on the zeroth order Hamiltonian is in order. It has been suggested[29] that setting the $\omega_k(s)$ equal to the value they take at the transition state for use in the zeroth order Hamiltonian will give a reasonable approximation to the multidimensional quantum system. In other words the effect of the bath degrees of freedom is simply to subtract a constant amount from the energy available for the scattering event. Some reflection will show that one cannot expect much from this approximation, but that it does reasonably mimic one aspect of the multidimensional problem. Schatz and Kupperman[10] have shown that if one compares threshold energies for the collinear, coplanar, and fully three dimension $H+H_2$ the differences are given roughly by the zero point energy of the quantized bending motions orthogonal to the symmetric and antisymmetric stretches. Thus the coplanar reaction has a threshold roughly $\frac{1}{2}\,\omega_k(s)$ (k=3,s=0) above that of the collinear, and the three dimensional reaction is displaced in threshold by roughly twice this amount. (We set $\hbar$ equal to one.) These bending motions are asymptotically rotations, and we will treat their character at greater length when we discuss the application of the system-bath model to $H+H_2$. We can immediately see, however, that at higher energies the foregoing approximation must be very poor. The

collinear $H+H_2$ reaction probability rises rapidly to one after threshold, while in three dimensions it is always much lower than one. No possible arguments can be supported which suggest that with the bath quantum numbers set to zero one must really interpret the zeroth order result as a sum over all bath states, and so treatment of the three dimensional problem as a pseudo-collinear one will fail at all but the lowest energies, and can give good results only because of good luck.

Now that we have our zeroth order Hamiltonian, we proceed to construct the first order correction to the transmission amplitudes. To do this we need zeroth order eigenfunctions. Like the transmission amplitudes, we choose them so that they will be diagonal in the bath quantum numbers:

$$f^{o}_{n',n}(s) = f_{n_2',n_2}{}^{n_3 n_4 \cdots} \delta_{n_3',n_3} \cdots \delta_{n_F',n_F}. \qquad \text{IIc-5}$$

These functions are obtained from a collinear like scattering calculation with boundary conditions appropriate to reaction path variables:

$$f_{n',n}(s) \sim \exp(ik_n s)/(k_n)^{1/2}\, \delta_{n',n} + \exp(-ik_n' s)/(k_n')^{1/2}\, r^{o}_{n',n}(E)$$

$$s \to -\infty \qquad \text{IIc-6a}$$

$$f_{n',n}(s) \sim \exp(ik_n' s)/(k_n')^{1/2}\, t^{o}_{n',n}(E). \qquad s \to \infty \qquad \text{IIc-6b}$$

Here r^o and t^o are the zeroth order reflection and transmission amplitudes. We will now derive the expression for the first order correction to these quantities. This is a technical, formal manipulation, but we include it for completeness. One dimensional formulae will make clear the necessary approach for the multi-dimensional case.

The Lipmann-Schwinger equation (IIa-7) has a direct analog for the scattering wavefunction:

$$\psi_k^+ = \phi_k^+ + G^{o+} V \psi_k^+. \qquad \text{IIc-7}$$

Here ψ_k^+ is the true scattering wavefunction matched to outgoing boundary conditions, ϕ_k^+ is the free wavefunction; and G^{o+} is the free Green function appropriate to outgoing boundary conditions. It is not hard to show that:

$$G^{o+}(x,x';k) = 2m \exp(ik|x-x'|)/2ik \qquad \text{IIc-8}$$

If we now take the limit of ψ_k^+ as x gets large and compare it to the result we know we physically have to get we obtain

$$\psi_k^+ \sim \exp(ikx)/(k)^{1/2}(1-im\langle\phi_k^+|V|\psi_k^+\rangle). \qquad \text{IIc-9}$$

Thus we find

$$t = (1-im\langle\phi_k^+|V|\psi_k^+\rangle). \qquad \text{IIc-10}$$

Taking the $x \to -\infty$ limit we see

$$r = -im\langle\phi_k^-|V|\psi_k^+\rangle. \qquad \text{IIc-11}$$

Here ϕ_k^- is just a plane wave moving in the opposite direction to ϕ_k^+. This could equally well be written ϕ_{-k}. We now proceed as in section IIa and note

$$t = 1-im\langle\phi_k^+|V+VG^+V|\phi_k^+\rangle \qquad \text{IIc-12a}$$

$$r = -im\langle\phi_k^-|V+VG^+V|\phi_k^+\rangle. \qquad \text{IIc-12b}$$

We now assume that we may divide the potential $V = V^o + V^1$. Define $G^o = (E-T-V^o)^{-1}$, and use IIa-7 truncated to first order in V^1 to obtain

$$V + VG^+V \cong V^o + V^oG^{o+}V^o + (1 + V^oG^{o+})V^1(1 + G^{o+}V^o). \qquad \text{IIc-13}$$

We let $t = t^o + t^1$ IIc-14a

$$t^o = 1 - im\langle\phi_k^+|V^o+V^oG^{o+}V^o|\phi_k^+\rangle \qquad \text{IIc-14b}$$

$$t^1 = -im\langle\phi_k^+|(1 + V^oG^{o+})V^1(1 + G^{o+}V^o)|\phi_k^+\rangle. \qquad \text{IIc-14c}$$

Similarly $r = r^o + r^1$ IIc-15a

$$r^o = im\langle\phi_k^-|V^o+V^oG^{o+}V^o|\phi_k^+\rangle \qquad \text{IIc-15b}$$

$$r^1 = -im\langle\phi_k^-|(1 + V^oG^{o+})V^1(1 + G^{o+}V^o)|\phi_k^+\rangle. \quad \text{IIc-15c}$$

If we use a Lipmann-Schwinger expression for scattering wavefunctions generated by the potential V^0 we find[30]

$$(1 + G^{o+}V^o)|\phi_k^+\rangle = |\psi_k^+\rangle \quad \text{IIc-16a}$$

$$\langle\phi_{+(-)}k|(1 + V^oG^{o+}) = \langle\psi_{+(-)k}^-|. \quad \text{IIc-16b}$$

This gives as a final form for our distorted wave transmission and reflection operators

$$t^1 = -im\langle\psi_k^-|V^1|\psi_k^+\rangle \quad \text{IIc-17a}$$

$$r^1 = -im\langle\psi_{-k}^-|V^1|\psi_k^+\rangle. \quad \text{IIc-17b}$$

A few more standard relations may be derived, and they can be found in Messiah's excellent text[31]. We here present them without proof.

$$\psi_{-k}^{+(-)}(x) = \psi_{+k}^{+(-)*}(x). \quad \text{IIc-18}$$

If the potential is symmetric about x=0, then

$$\psi_{-k}^+(x) = \psi_k^+(-x). \quad \text{IIc-19}$$

This last identity is obvious upon reflection. It simply says that if the potential is symmetric, moving forward through positive x is

equivalent to moving backwards through negative x. We now have all the tools we need to construct the general form of the first order transmission matrix. Everything we have written with respect to one dimensional scattering wavefunctions applies directly to our multidimensional scattering wavefunctions. The only difference is that now the wavefunctions are also labeled by initial and final quantum states rather than just initial and final wavevectors. Recall that all bath quantum numbers will be conserved to zeroth order. Setting mass to 1 we may immediately write

$$t^1{}_{n',n} = -i\sum_{n''',n''} \int ds\, f^-{}_{n''',n'}(s)^* \, H^1{}_{n''',n''} \, f^+{}_{n'',n}(s) \quad \text{IIc-20}$$

where $H^1{}_{n''',n''}$ is the matrix of H^1 in the vibrationally adiabatic basis of transverse vibrational states. Again we use n as a composite symbol for the entire set of quantum numbers. If specific quantum numbers are referred to we will always indicate this explicitly. H^1 is still a multiplicative and differential operator in the reaction coordinate degree of freedom. The adiabaticity of the zeroth order Hamiltonian mentioned before allows us to simplify this to the following

$$t^1{}_{n',n} = -i\sum_{n_2''',n_2''} \int ds\, f^{-n_3'\ldots n_F'}{}_{n_2''',n_2'}(s)^* \, H^1{}_{n_2'''n_3'\ldots n_F',n_2''n_3\ldots n_F} \, f^{+n_3\ldots n_F}{}_{n_2'',n_2}(s). \quad \text{IIc-21}$$

Before we proceed to a specific application, it is an appropriate time to make a few general comments. The first is that the work of

this section is completely general and certainly need not be restricted to the reaction path Hamiltonian. One needs a coordinate system which allows a clear choice as to which of the modes are strongly coupled and which are weakly coupled. Of course, the goal is to choose a zeroth order Hamiltonian which is easy to solve and yet still is close to being exact. The great success of hyperspherical[32] coordinates suggests that another possible division of the coordinates would be to use exact hyperspherical coordinates for a two dimensional problem plus adiabatic oscillators (gotten by a numerical solution of a one dimensional Schrodinger equation for various values of the hyperradius) for the zeroth order Hamiltonian. The other comment is to again emphasize that as long as the system is restricted to two degrees of freedom, as the physical size of the reaction gets larger (i.e., the number of atoms increases), the implementation of this approach does not get much more difficult. Because the bath degrees of freedom are treated as adiabatic harmonic oscillators, it turns out that only one integration, that over the s degree of freedom, need be done numerically. We also point out that it is exactly as the size of the reaction gets larger that we expect a system-bath decomposition to become more accurate.

d - Application to $H+H_2$ - Preliminaries

With this formal apparatus built up we now proceed to application of the theory[33]. We wish to test the theory against accurate, exact quantum calculation. We are therefore forced to use

the theory for exactly the kind of system for which it was not created to study. We shall study the rotationally inelastic reactive scattering in three dimensions of $H+H_2$. This is certainly as "unpolyatomic" as a reaction can get, but as stated in the introduction, this is the only reaction for which accurate three dimensional state-to-state quantum scattering data exist. There are not many modes in an atom-diatom reaction; so we don't have too much latitude as to what we choose for the system and what we choose for the bath. We here choose the system to be composed of the reaction coordinate plus the symmetric-like stretch vibrational mode which is orthogonal to the reaction path. Since the reaction path is collinear, this means that the system is just the normal collinear $H+H_2$ degrees of freedom. The bath is then made up of the two other vibrational modes orthogonal to the reaction path. Within the strong interaction region, these are bends, and asymptotically they have zero frequencies. This means that they are asymptotically rotations, and we will present an analysis to show how these bends are related to the more commonly considered rotations. We will show that even within the first order perturbative treatment, very accurate results are obtained when compared to the exact quantum results of Schatz and Kuppermann[10]. Again we stress that this approach was intended for large systems of a truly polyatomic character, but the results we will obtain will provide ample justification for a sanguine attitude toward further application.

e - A Bath of Bends

We recall that equations IIb-2c and IIb-2d gave the first order perturbative coupling between the system and the bath if we ignore adiabatic coupling induced by frequency variation along the reaction path. These perturbations depended on the coupling elements $B_{k,k'}(s)$ between the bath degrees of freedom and the system. As we mentioned in the last section, for the $H+H_2$ reaction, for total J=0 one has four modes. We label, as always, the reaction coordinate as mode 1, and the symmetric stretch (which is asymptotically the vibrational motion of a hydrogen molecule) as mode 2. Modes 3 and 4 are the degenerate bends of the bath. Because of symmetry, however, the only off-diagonal coupling elements are between the reaction coordinate and the symmetric stretch. These are just the collinear degrees of freedom. We do know that there is coupling between different rotational states in the three-dimensional reaction; so there must be some kind of coupling between the reaction coordinate and the bends. This is, of course, provided by adiabatic coupling of the bends to the reaction path through variation in the bath frequency as a function of position along the reaction coordinate. We gave in formula IIb-2d a classical expression for this coupling. It was also pointed out at that time that this formula was the result of a transformation to a mixed classical representation, and so direct conversion to a quantum mechanical operator is not possible. To find the quantum mechanical nature of this effect we use the form of distorted wave analysis provided by Miller.

$$t^{1}{}_{n_2'n_3'n_4',n_2n_3n_4} = \langle \chi^{-}{}_{n_2'n_3'n_4'} | H - E | \chi^{+}{}_{n_2n_3n_4} \rangle . \quad \text{IIe-1}$$

Here $\chi^{-(+)}{}_{n_2n_3n_4}$ are distorted waves which are functions of the system variables s and Q_2, and also of the bath variables Q_3 and Q_4. To zeroth order we assume no adiabatic coupling between the bath and the system; so we must choose for our distorted waves a direct product of system scattering wavefunctions and adiabatic bound states for the bath degrees of freedom, to wit:

$$\chi^{-(+)}{}_{n_2n_3n_4} = \Xi^{-(+)n_3n_4}{}_{n_2}(s,Q_2)\ \phi_{n_3}(Q_3;s)\ \phi_{n_4}(Q_4;s). \quad \text{IIe-2}$$

The functions $\Xi^{-(+)n_3n_4}{}_{n_2}(s,Q_2)$ are the solutions of the collinear-like Schrodinger equation. More concretely, they are solutions of the quantum mechanical Hamiltonian H_o:

$$H_o = -\tfrac{1}{2}\,[(1/\eta)^{1/2}\ \partial/\partial s\ (1/\eta)\ \partial/\partial s\ (1/\eta)^{1/2} +$$

$$(1/\eta)^{1/2}\ \partial/\partial Q_2\ (\eta)\ \partial/\partial Q_2\ (1/\eta)^{1/2}\,] + \tfrac{1}{2}\,\omega_2(s)^2 Q_2{}^2 +$$

$$(n_3 + n_4 + 1)\omega_{bath}(s) + V_o(s) \qquad \text{IIe-3}$$

where $\eta = 1+B_{2,1}(s)Q_2$, and as always we set $\hbar$ equal to one. This quantum mechanical operator is obtained by direct application of Podolsky's method[23]. The vibrational functions $\phi_{n_{3,4}}(Q_{3,4};s)$ are the adiabatic harmonic oscillator functions for the degenerate bends. One must, of course, perform a reaction path calculation on the potential

energy surface to obtain the frequencies and coupling element as a function of position along the reaction path. Scattering boundary conditions are applied to the solutions $\Xi^{-(+)n_3n_4}{}_{n_2}(s,Q_2)$ as outlined in the last section.

The starting point for our calculation is then the solution of the collinear scattering problem. This is by far the hardest numerical part of the whole procedure; and so we will discuss our solution in some detail. We implemented the method of Wu and Levine[34]; and so we will not go through a rederivation of all their formulae. There is a well known problem associated with the natural collision coordinates method (i.e., collinear reaction path Hamiltonian systems). In the region of high curvature it can happen that the term $1+B_{2,1}(s)Q_2$ goes through a zero; and hence the differential equation, which depends on $(1/\eta)$, will be rather poorly behaved. This problem is eliminated by including a factor of η^4 in the coupled channel expansion of the wavefunction:

$$\Xi^{-(+)n_3n_4}{}_{n_2}(s,Q_2) = \eta^4\sum_{n_2'} \phi_{n'_2}(Q_2;s)\, f^{n_3n_4-(+)}{}_{n_2'n_2}(s). \quad \text{IIe-4}$$

Again, $\phi_{n_2}(Q_2;s)$ is an adiabatic harmonic oscillator function, this time for the symmetric stretch degree of freedom. The coupled channel equations for the translational function $f^{n_3n_4-(+)}{}_{n_2,n_2}(s)$, determined by substituting expansion IIe-4 into the Hamiltonian IIe-3, are exactly those given by Wu and Levine. The actual numerical integration of the close-coupled equations was achieved with a variable step size, variable order version of the Adams-Pece

integrator. We consider only ground vibrational state scattering, and at these energies, it is enough to include five channels in the coupled channel problem. This is rather innocuous sounding; and so at this point it is worth mentioning what this implies about the actual computation. When one chooses a five channel expansion, one really has a five-by-five matrix of initial and final vibrational states. This immediately results in twenty-five coupled second order differential equations. Codes exist only to solve first order equations, and so it now becomes fifty coupled first order equations. Finally, since one doesn't know the physical boundary conditions (these are exactly the transmission and reflection amplitudes we are trying to get), one simply propagates two linearly independent solutions and matches to the physical boundary conditions asymptotically. Thus, our five channel problem translates into the propagation of one hundred coupled differential equations. Before we depart from these technical aspects, we note that one can use any method available to obtain the distorted wavefunctions. Direct integration (rather than R-matrix propagation with subsequent integration of the physical boundary conditions) was simply the most convenient method available.

We are now ready to form the transition matrix. It is easy to see from the form of the Hamiltonian operator that we have a selection rule on bath transitions:

$$(\Delta n_3, \Delta n_4) = (\pm 2, 0)\ ,\ (0, \pm 2). \qquad \text{IIe-5}$$

This is because transitions in the bath are gotten from terms like

$$\partial/\partial s\ \phi_{n_3}(Q_3;s) = \omega_3'(s)/2\ \omega_3(s)[(n_3(n_3-1))^{1/2}\phi_{n_3-2}(Q_3;s)$$

$$-\tfrac{1}{2}((n_3+1)(n_3+2))^{1/2}\ \phi_{n_3+2}(Q_3;s)]. \qquad \text{IIe-6}$$

This implies

$$\langle \phi_{n_3}|\ \partial/\partial s\ \phi_{n_3}\rangle = \omega_3'(s)/4\ \omega_3(s)\ [(n_3(n_3-1))^{1/2}\ \delta_{n_3',n_3-2}$$

$$-((n_3+1)(n_3+2))^{1/2}\ \delta_{n_3',n_3+2}]. \qquad \text{IIe-7}$$

These terms produce the exact quantum mechanical analog of the classical expression IIb-2d with the exact same coupling element $\omega_3'(s)/2\ \omega_3(s)$, equation IIb-2e.

Since we only deal with the ground vibrational state, the only final states for which the first order correction is non-zero are

$$(n_2',n_3',n_4') = (0,0,2) \text{ and } (0,2,0). \qquad \text{IIe-8}$$

The zeroth order transmission amplitude is diagonal in bath quantum numbers; so there is no zero order contribution to these terms. We thus study the quantity

$$|t^1{}_{002,000}(E)|^2 + |t^1{}_{020,000}(E)|^2 = 2|t^1{}_{002,000}|^2. \qquad \text{IIe-9}$$

We have now to relate this quantity to that calculated in a more standard full coupled channel calculation. The question is how to relate the reaction probability labeled by the bending quantum numbers (n_3,n_4) to the more standard ones labeled by the initial and final rotational quantum numbers (j,k). j is the asymptotic rotational quantum number of H_2 and k is the component of rotation along the relative velocity vector, or the helicity. The correlation is not one-to-one, and so the only truly rigorous relation between the two reaction probabilities is an equality between total reaction probability. In other words

$$\sum_{j'k'}\left|S^{J=0}_{0j'k',000}\right|^2 = 2\sum_{n_3'n_4'}\left|t_{0n_3'n_4',000}\right|^2. \qquad \text{IIe-10}$$

We include a 2 in the right side of this equation because the system-bath approach describes reaction of a hydrogen atom with a specific side of the hydrogen molecule. For J=0 one must have k=0 so that to second order in transition matrices IIe-10 yields

$$\sum_j\left|S^{J=0}_{0j0,000}\right|^2 = 2\left[\left|t^0_{000,000}\right|^2 + 2\mathrm{Re}(t^{2*}_{000,000}t^0_{000,000})\right]$$

$$+ 4\left|t^1_{002,000}\right|^2. \qquad \text{IIe-11}$$

We assume that it is probably not a bad idea to identify the rotationally elastic terms on both sides of the equations. In other words we assume that in both representations ground states correlate fairly well with each other. It is difficult to provide rigorous

numerical support for this correlation because $t^2_{020,000}$ would have to be calculated, and this is an extremely hard quantity to obtain. Approximating the j=0 term with the zeroth order term alone (i.e., the collinear-like term) is equivalent to a model proposed by Bowman[29], and as we have already discussed; at all but the lowest energies this is a very poor approximation. The correlation we employ for the ground states is also implied by the work of Harms and Wyatt[35]. So with this final approximation we obtain

$$4\left|t^1_{002,000}(E)\right|^2 \cong \sum_{j=1}^{\infty} \left|S^{J=0}_{0j0,000}\right|^2. \quad \text{IIe-12}$$

It might at this point be argued that the theory is no longer state specific because we have to sum over the normal rotational states to obtain a comparison. This argument might have some validity, but again we stress this is not a theory which is designed to deal with $H+H_2$. We are forced to sum over rotational states only because we wish to compare the numerical accuracy of our theory with exact close coupled results. For a large system for which there is no possibility of a true state-to-state calculation, the theory would be used to provide general quantum features of the effect of the bath. In large systems, much of the bath would be true vibrations, and all these correlation problems are moot in that case - the adiabatic harmonic functions would be expected to be extremely close to the "physical" final quantum states. Thus the ambiguity is at least partly a result of the problem we are forced to treat.

We give for completeness the final formula obtained from

substitution of the wavefunction form IIe-2 into equation IIe-1.

$$(7/2)(1/\sqrt{\mu})\langle\sum_{n_2'''} f^{02(+)}_{n_2''',0}(-s)\ \phi_{n_2'''}(Q_2;s)\ \phi_{n_3=2}(Q_3;s)|$$

$$\eta^6 B'_{2,1} Q_2|\ \sum_{n_2''} f^{02(+)}_{n_2'',0}(s)\ \phi_{n_2''}(Q_2;s)\ \partial/\partial s(\ \phi_{n_3}(Q_3;s)_{n_3=0})\rangle$$

$$+\ (1/\sqrt{\mu})\langle\sum_{n_2'''} f^{02(+)}_{n_2''',0}(-s)\ \phi_{n_2'''}(Q_2;s)\ \phi_{n_3=2}(Q_3;s)|\eta^7|$$

$$\sum_{n_2''} d/ds(f^{02(+)}_{n_2'',0}(s))\ \phi_{n_2''}(Q_2;s)\ \partial/\partial s(\ \phi_{n_3}(Q_3;s)_{n_3=0})\rangle +$$

$$(1/\sqrt{\mu})\langle\sum_{n_2'''} f^{02(+)}_{n_2''',0}(-s)\ \phi_{n_2'''}(Q_2;s)\ \phi_{n_3=2}(Q_3;s)|\eta^7|$$

$$\sum_{n_2''} f^{02(+)}_{n_2'',0}(s)\ \partial/\partial s(\phi_{n_2''}(Q_2;s)\ \partial/\partial s(\ \phi_{n_3}(Q_3;s)_{n_3=0})\rangle. \qquad \text{IIe-13}$$

Here we have used the fact that because the reaction, and so the potential, is symmetric

$$f^-(s)^* = f^+(-s) \qquad \text{IIe-14}$$

and μ is the reduced mass of the $H+H_2$ system.

f - Results

We use the Porter-Karplus potential energy surface[36] because it was the one used by Schatz and Kuppermann[10]. In figure I we show the coupling elements $B_{2,1}(s)$ (the curvature coupling) and $B_{3,3}(s)$ (the adiabatic coupling). The coupling $B_{2,1}(s)$ is what couples the

symmetric stretch to the reaction path, and we treat it exactly as part of the system. Because of the symmetry of the system $B_{3,3}(s) = B_{4,4}(s)$. Since we treat this coupling perturbatively, we would hope that it is much smaller than the curvature coupling. While it is smaller at all points along the reaction path, it is not remarkably so, and as a matter of fact after ten mass weighted atomic units (about .25 Bohr in conventional units) the two couplings are practically equal.

The results of our calculation are shown as the solid line in figure II. (i.e., the result of four times the square of equation IIe-13). The only place where definite comparison to the results of Schatz and Kuppermann[10] can be made is at .60 eV. At this energy exact results exist for the transitions $j=0\rightarrow1$, $0\rightarrow2$, and $0\rightarrow3$; and so we can sum these in order to obtain comparison to the system bath model. (Higher transition probabilities are effectively zero at this energy.) As can be seen, the agreement is essentially exact at this energy. At lower energies we feel our results probably fall too slowly. This might be due to the fact that at lower energies, the region of the potential past ten mass weighted atomic units will exert a greater influence over the outcome of the reaction. We recall that it was here that the two couplings were essentially equal.

We have now seen that a perturbative treatment can work quite well, even for a system as small as $H+H_2$. At the beginning of this section we mentioned that this was a method which studied coupling between degrees of freedom rather than coupling between states. In a way this is not the case because coupling between degrees of freedom

simply implies that direct product basis functions will not diagonalize the scattering Hamiltonian; and so there will be a coupling between these states. We feel this distinction rests in semantics, and the model retains its intuitive physical appeal. As a final suggestion for future work beyond the state specific work mentioned in this chapter we note that this study was originally undertaken in order to understand and extend the correlation function approach to scattering first proposed by van Hove[37]. The standard correlation function approach uses the Born approximation and is very useful for investigations of such problems as the scattering of thermal neutrons from liquids. (In this case the wavefunctions of the neutrons are well represented by free particles before and after the scattering.) It was our wish to implement an extension for chemical reactions. When we realized how accurate the theory might prove, we decided to pursue a state to state calculation. Recently Cerjan and co-workers[38] have proposed just such a use of the correlation function formalism coupled with the Distorted Wave Born approximation. A unification of the two approaches could prove very useful.

III - Quantum Mechanical Rate Constants

a - Introduction

In the second chapter of this dissertation we presented an approximate theory to obtain state-specific quantum mechanical reactive scattering data. As was pointed out, this is certainly the most detailed information one can look for from a Born-Oppenheimer potential energy surface. In this section we take an exactly opposite tack - we attempt no approximation, but we don't seek such detailed information. We attempt to develop a methodology to evaluate the exact quantum mechanical rate constant for a bi-molecular reaction. In all that follows we will use the terms rate constant and Boltzmann rate constant interchangeably. By Boltzmann rate constant we assume the reactants to be always in a Boltzmann distribution in all internal, translational, and rotational degrees of freedom. Following Levine and Bernstein's[39] language, we assume there are no disequilibrium effects, or in other words, as reactants are depleted, they are always replaced in such a manner as to maintain a Boltzmann distribution. Within the rigorous definition of the rate constant

$$k = \langle v \sigma \rangle \qquad \text{IIIa-1}$$

where the average indicated is over the Boltzmann distribution.

Scattering theorists always tend to think in terms of state to state data; so we might at this point ask if there is any point to

the construction of a new formal edifice devoted to direct calculation of an average quantity such as the rate constant. We obviously feel that the question may be answered in the affirmative: the rate constant is most often the quantity of interest to the experimentalist. The reason for this is certainly that this is the quantity most related to the real world (and not incidentally, the most observable). One does not often encounter a supersonic expansion of state selected reactants in nature. It is crucial to understand the microscopic details of chemical reactions, but it is also very hard to do. Just as only a handful of theorists can perform exact quantum, state-to-state scattering calculations, so too can only a few experimentalists measure state to state cross sections. At the moment only $H+H_2$[40] and H_2+F[41] have been studied in such detail.

Up to this time, the only way theorists had to determine exact rate constants was to first perform a state-specific calculation and then to average over a Boltzmann distribution. We were motivated in this work by the notion that this can't possibly be the best way to proceed. (An experimentalist would never think of building a molecular beam apparatus only then to use the information it produced to average to a Boltzmann rate constant.) It should be pointed out that an extremely elegant theory does exist to construct approximate rate constants within the classical framework: the transition state theory[42]. The problem is that it is an inherently classical and not quantum mechanical theory. A huge number of attempts have been made to patch onto this theory a quantum mechanical language, but none has been too sucessful, and many are totally non-rigorous[43]. The theory

here presented will start from the language of transition state theory, but all derivations will be perfectly rigorous quantum mechanics. It is also our hope that by following the philosophy of transition state theory, one of the main assumptions of transition state theory will work to our advantage. Transition state theory is a zero time limit approximation to classical dynamics. Thus it will be our hope that we need follow quantum dynamics for only a short period of time. These various ideas will be demonstrated and applied as the derivations proceed in the following sections.

b - Definition of a Quantum Mechanical Rate Constant

Using equation IIIa-1 it is not hard to show that the Boltzmann rate constant may be written in the form

$$k_{b\leftarrow a} = (k_b T/h) Q_a^{-1} \sum_{n_a, n_b} \int_0^\infty d(\beta E_1) e^{-\beta(E_1+\varepsilon_{n_a})} \left| S_{n_b, n_a}(E_1) \right|^2 . \quad \text{IIIb-1}$$

Here k_b is Boltzmann's constant; T is the temperature; β is $1/k_b T$; E_1 is the translational energy of the reacting bimolecular system; and ε_{n_a} is the internal energy of the reactants. The label a is a general one which refers to the reactant channel arrangement of the atoms and b refers to the product channel arrangement. n_a and n_b are all the quantum numbers necessary to describe the respective arrangements. Q_a is the partition function for reactants. Following Miller[44], all derivations will proceed in a two dimensional world (that is a collinear atom-diatom scattering problem), but extension to higher

(or lower) dimensionality will be obvious. Suppose we define a coordinate system on the potential energy surface (R,r), and place a dividing surface at $R = R_o$ in the reactant channel. (See figure III.) If $\psi(r,R)$ is the scattering wavefunction on the potential, then the flux through the surface is given by

$$-\mathrm{Re} \int_{-\infty}^{\infty} dr\ \psi(r,R)^{*}(\hbar/i\mu)\ \partial/\partial R\ \psi(r,R)\Big|_{R=R_o} \qquad \text{IIIb-2}$$

where μ is the mass associated with the R degree of freedom. Now we know that in the reactant region, the scattering wavefunction must be of the form

$$\psi_{n_a}(r,R) \sim \exp(-ik_{n_a}R)/(k_{n_a})^{1/2} * \phi_{n_a}(r) +$$

$$\sum_{n_a'} \exp(+ik_{n_a'}R)/(k_{n_a'})^{1/2}\, \phi_{n_a'}(r)\ (v_{n_a}/v_{n_a'})^{1/2}\, S_{n_a',n_a}(E). \qquad \text{IIIb-3}$$

If this form is substituted into IIIb-2 it is not hard to show that the flux takes the form

$$(v_{n_a}/h)[\ 1 - \sum_{n_a'} |S_{n_a',n_a}(E_1)|^2\ ]. \qquad \text{IIIb-4}$$

Similarly, the asymptotic form of the wavefunction in the product channel is

$$\psi_{n_a}(r,R) \sim \sum_{n_b} \exp(+ik_{n_b}R)/(k_{n_b})^{1/2}\, \phi_{n_b}(r) *$$
$$(v_{n_a}/v_{n_b})^{1/2} * S_{n_b,n_a}(E). \qquad \text{IIIb-5}$$

Using this equation in IIIb-2 we can also show that the flux is equal to

$$(v_{n_a}/h)\ \sum_{n_b}|S_{n_b,n_a}(E_1)|^2. \qquad \text{IIIb-6}$$

Of course this has to be true because

$$\sum_{n_a'}|S_{n_a',n_a}(E_1)|^2 + \sum_{n_b}|S_{n_b,n_a}(E_1)|^2 = 1. \qquad \text{IIIb-7}$$

In other words, the total probability to react plus the total probability not to react must be unity. We have also shown that the total flux through a surface in the entrance channel is equal to the total flux through a surface in the exit channel. In fact, it's not hard to show that it dosen't matter where we put the surface. For a general surface defined by the equation

$$f(r,R) = 0 \qquad \text{IIIb-8}$$

$$\text{flux} = \text{Re} \int_{-\infty}^{\infty} drdR\ \delta[f(r,R)]\ \psi^*(r,R)(\ \partial/\partial r\ f(r,R),\ \partial/\partial R\ f(r,R))$$

$$\cdot\ ((\hbar/im_r)\ \partial/\partial r\ ,(\hbar/im_R)\ \partial/\partial R)\ \psi(r,R). \qquad \text{IIIb-9}$$

We define a flux operator for a general set of coordinates {q} as

$$F = \delta[f(q)][\partial/\partial q(f(q))]\cdot v\ ;\ v_k=(\hbar/m_{q_k})\ \partial/\partial q_k. \qquad \text{IIIb-10}$$

Using all this information we can, once again following Miller[44], form a relation between the sum over scattering matrix elements and the matrix elements of this flux operator:

$$(1/h)\ \sum_{n_b}\left|S_{n_b,n_a}(E_1)\right|^2 = (1/v_{n_a})\mathrm{Re}\langle\psi_{n_a}|F|\psi_{n_a}\rangle. \quad \text{IIIb-11}$$

(v_{n_a} is again just a number, not the velocity operator.) This allows us to write

$$k_{b\leftarrow a} = \mathrm{Re}Q_a^{-1}\sum_{n_a}\int_0^{\infty}d(E_1)e^{-\beta(E_1+\varepsilon_{n_a})}(1/v_{n_a})\langle\psi_{n_a}|F|\psi_{n_a}\rangle. \quad \text{IIIb-12}$$

So far we haven't made very much progress in eliminating reference to the state-to-state scattering data - we have simply eliminated the scattering matrix elements in favor of the scattering wavefunction. Noting that ψ_{n_a} is an eigenfunction of the full Hamiltonian and changing the variable of integration to p we obtain

$$k_{b\leftarrow a} = \mathrm{Re}Q_a^{-1}\sum_{n_a}\int_{-\infty}^{0}\langle\psi_{n_a,p}|Fe^{-(\beta H)}|\psi_{n_a,p}\rangle dp. \quad \text{IIIb-13}$$

We include a subscript of p on the scattering wavefunction in order to emphasize that it is equally well a function of momentum as a function of energy. Note that the strange negative range for the momentum simply arises because reaction is in the negative R direction. We will later use coordinates in which this is not the case, but the reader will be given ample warning of the switch. We now note that if we could integrate over all p the integral would be

a trace; and so we would not need to consider the scattering wavefunctions, because the trace is independent of the basis employed. In order to do that we need only include a projection operator that projects only onto the reactive momentum state. That is

$$\mathbf{P}|\psi_{n_a},p\rangle = |\psi_{n_a},p\rangle \qquad p<0$$
$$\mathbf{P}|\psi_{n_a},p\rangle = 0 \qquad p>0. \qquad \text{IIIb-14}$$

The obvious form for $\mathbf{P}$ is

$$\mathbf{P} = \sum_{n_a} \int_{-\infty}^{\infty} dp\ h(-p)|\psi_{n_a},p\rangle\langle\psi_{n_a},p| \qquad \text{IIIb-15}$$

and with this

$$k_{b\leftarrow a} = Q_a^{-1}\mathrm{tr}[e^{-\beta H}\mathbf{FP}]. \qquad \text{IIIb-16}$$

This expression derived by Miller[44] is the starting point for our derivations. First it is useful to put the projection operator in a slightly different form. For simplicity and directness of application to later work we now assume that the reactive direction is in the positive momentum direction. We first recognize that because $|\psi_{n_a},p\rangle$ is a scattering eigenfunction, it is related to the free scattering function through the Moller operator:

$$|\psi_{n_a},p\rangle = \lim_{t\to\infty} e^{iHt/\hbar} e^{-iH_o t/\hbar} |\phi_{n_a},p\rangle = \Omega^- |\phi_{n_a},p\rangle. \qquad \text{IIIb-17}$$

It is clear then that

$$\mathbf{P} = \lim_{t\to\infty} e^{iHt/\hbar} e^{-iH_o t/\hbar} \mathbf{P}_o e^{iH_o t/\hbar} e^{-iHt/\hbar} \qquad \text{IIIb-18}$$

where $\mathbf{P}_o$ is simply equation IIIb-15 with $|\psi_{n_a,p}\rangle$ replaced be $|\phi_{n_a,p}\rangle$. $\mathbf{P}_o$ commutes with H_o so

$$\mathbf{P} = h(p(t\to\infty)). \qquad \text{IIIb-19}$$

We emphasize that p in equation IIIb-19 is an operator. The argument of the operator simply means that it is the Heisenberg evolved operator in the limit of large time. Thus our new form for the quantum mechanical projection operator is simply that operator which selects states which in infinite future are moving in the reactive direction. This is exactly what we might have expected. For clarity we switch the variable name to s; and the reader will want to picture variables in which +s is the reactive direction.

One final preliminary step is useful in order to put the rate expressions in a form which is easy to study. We now prove that it is possible to replace $h(p(t\to\infty))$ by $h(s(t\to\infty))$ in the form for the projection operator. This is reasonable on reflection - it says that if in the infinite future we have passed the "transition state" then we must have reacted. (As we will see in the mathematical proof the qualification that this must occur in the infinite future is the crucial point. Logically this is also what we might expect. At any time "before infinity" we can always come back and recross the

barrier. If this were not the case then transition state theory would always be exact in the classical limit. We point out that if there is a resonance in the entrance channel we can be delayed on one side of the barrier, but this delay time can not be infinite. Were this the case we would have a bound state.) We take note that the operators

$$\mathbf{P}_s = \exp(iHt/\hbar)h(s)\exp(-iHt/\hbar) \qquad \text{IIIb-20a}$$

$$\mathbf{P}_p = \exp(iHt/\hbar)h(p)\exp(-iHt/\hbar) \qquad \text{IIIb-20b}$$

may be rewritten as the operators

$$\mathbf{P}_s = \Omega^- \exp(iH_o t/\hbar)h(s)\exp(-iH_o t/\hbar)\ \Omega^{-+} \qquad \text{IIIb-21a}$$

$$\mathbf{P}_p = \Omega^- \exp(iH_o t/\hbar)h(p)\exp(-iH_o t/\hbar)\ \Omega^{-+} \qquad \text{IIIb-21b}$$

where Ω^- is the Moller wave operator given in equation IIIb-17. It is a standard result that the Moller operator takes a limit[45] (i.e., matrix elements of the operator are bounded); it is therefore the case that inserting a few complete sets of states will allow us to just consider the operators

$$\mathbf{P}_s' = \exp(iH_o t/\hbar)h(s)\exp(-iH_o t/\hbar) \qquad \text{IIIb-22a}$$

$$\mathbf{P}_p' = \exp(iH_o t/\hbar)h(p)\exp(-iH_o t/\hbar). \qquad \text{IIIb-22b}$$

Taking a coordinate matrix element, and using the fact

$$\langle s|p\rangle = (2\pi i\hbar)^{-1/2}\exp(ips/\hbar) \qquad \text{IIIb-23}$$

it is not hard to show that

$$\langle s'|\mathbf{P}_p'|s\rangle = (2\pi\hbar)\int_0^\infty \exp(ip(s'-s)/\hbar)dp. \qquad \text{IIIb-24}$$

For the coordinate representation of the position projector, one obtains:

$$\langle s'|\mathbf{P}_s'|s\rangle = \int_0^\infty ds''\langle s'|\exp(iH_o t/\hbar)|s''\rangle$$

$$* \langle s''|\exp(-iH_o t/\hbar)|s\rangle. \qquad \text{IIIb-25}$$

The free particle propagator is given by

$$\langle s''|\exp(iH_o t/\hbar)|s''\rangle = (m/(2\pi i\hbar t))^{1/2}\exp[im(s''-s)^2/(2\hbar t)] \qquad \text{IIIb-26}$$

We obtain for this matrix element

$$\langle s'|\mathbf{P}_s'|s\rangle = \exp[(im/2\hbar t)(s^2-s'^2)](2\pi\hbar)\ x$$

$$\int_0^\infty dp\ \exp(ip(s'-s)/\hbar). \qquad \text{IIIb-27}$$

We thus see that in the infinite time limit, the two operators are in

fact equal. Before we proceed, we wish to point out one caveat for those who are interested in future work in this area. In a reacting system it may be desired to use a curvilinear coordinate system like the reaction path Hamiltonian. If that is the case the preceeding proof does not necessarily hold. The reason is that in this type of system, the metric tensor has elements which are functions of the position coordinates, and it is not clear, for instance, that equation IIIb-23 holds. This is a manifestation of the same difficulty which prevents one from writing the Hamiltonian for such a system as

$$H = \sum_k P_k^2/(2m_k) + V \quad ; \; P_k = -i\hbar\, \partial/\partial q_k . \qquad \text{IIIb-28}$$

It may well be that a very similar subsitution as $h(p) \rightarrow h(s)$ is possible, but further investigations of the exact form of this subsitution will be needed. One might be missing stray factors of the Jacobean determinant of the transformation. Again, further investigations of this matter are necessary.

c - Alternate Forms of the Rate Constant

We are now ready to manipulate our rate expression so that it is in a form slightly more amenable to use. The first change is to cast it in terms of a symmetric, complex time. To do this, note that the operator $e^{-\beta H}$ must commute with the projection operator P. (It is easiest to see if we consider this before we replace h(p) with h(s).)

This must be because **P** was originally composed of eigenfunctions of the Hamiltonian H, and it is clear that

$$[f(A),g(\psi)] = 0 \text{ if } A\psi = a\psi. \qquad \text{IIIc-1}$$

Thus we can write our rate expression in the more symmetric form

$$k = (1/Q_a)\mathrm{Re}[\mathrm{tr}(F \exp(-\beta H/2)\ \mathbf{P} \exp(-\beta H/2))]. \qquad \text{IIIc-2}$$

Leaving **P** expressed in terms of h(p) we obtain

$$k = (1/Q_a)\lim_{t\to\infty} \mathrm{Re}[\mathrm{tr}(F \exp(iH/\hbar(t+i\hbar\beta/2))h(p)$$

$$\exp(-iH/\hbar(t-i\hbar\beta/2))]. \qquad \text{IIIc-3}$$

We may now define a complex time

$$t_c = t - i\hbar\beta/2. \qquad \text{IIIc-4}$$

We emphasize that this complex time is to have no physical meaning attached to it - it simply makes the equation look more symmetric, and hence will aid in the evaluation of the formulae later.

It is not hard to show that in order to obtain the real part of these operators, one need only replace the flux operator with a symmetrized version. If we place our dividing surface at s = 0, then this symmetrized version (as we might have expected) is

$$\bar{F} = \tfrac{1}{2}(F + F^{+}) = \tfrac{1}{2}(\delta(s)p_s/m + p_s/m\delta(s)). \qquad \text{IIIc-5}$$

If we now make use of the fact that we can replace h(p) by h(s) in the infinite time limit, we have for our rate expression

$$k = (1/Q_a)\lim_{t\to\infty} \mathrm{tr}[\bar{F}\exp(-iHt_c/\hbar)h(s)\exp(iHt_c^{*}/\hbar)]. \qquad \text{IIIc-6}$$

This is of course a statistical mechanical correlation function. It correlates the flux across the dividing surface at time t = 0 (real time) with being on the product side of the barrier at t large. This quantity is not obviously identifiable with the rate, but some of its derivative forms to be obtained shortly will turn out to be expressions we might have guessed. We would like to point out here that we are certainly not the first ones to relate quantum mechanical rates to statistical mechanical correlation functions. Many authors have taken this kind of tack, and we will not attempt a review of all previous work[46]. All are based on exact physics, and so should be exact, but we feel that our forms admit the clearest interpretation and simplest application.

In order to proceed, note that the argument of the limit in equation IIIc-6 is strictly zero at time t = 0. This is simple to see if one returns to the unsymmetrized form of k when one had to take the real part. At t = 0 all operators except for the flux operator are strictly real. The flux operator is purely imaginary, so that at time t = 0 the real part of the entire expression must be zero. It is

thus possible to rewrite IIIc-6 as

$$k = (1/Q_a)\mathrm{tr}[\bar{F}\exp(-iHt_c/\hbar)h(s)\exp(iHt_c^*/\hbar)]\Big|_0^\infty \qquad \text{IIIc-7}$$

In other words we can identify an operator $C_f(t)$ such that

$$k = (1/Q_a)\int_0^\infty dt\, C_f(t) \qquad \text{IIIc-8a}$$

$$C_f(t) = (d/dt)\mathrm{tr}[\bar{F}\exp(iHt_c/\hbar)h(s)\exp(iHt_c^*/\hbar)]. \qquad \text{IIIc-8b}$$

The time derivative can be taken inside the trace operation, and the derivative formally taken to yield

$$C_f(t) = (i/\hbar)\mathrm{tr}\{\bar{F}\exp(iHt_c/\hbar)[H,h(s)]\exp(iHt_c^*/\hbar)\}. \qquad \text{IIIc-9}$$

The commutator in the brackets can be easily evaluated. The potential (which, of course, is only a function of the position) must commute with h(s). Thus we evaluate

$$[p^2/(2m),h(s)] = (1/2m)(p[p,h(s)] + [p,h(s)]p) =$$

$$(\hbar/i)\,{}^1\!/_2\,(\delta(s)p_s/m + p_s/m\delta(s)). \qquad \text{IIIc-10}$$

This remarkable result once again yields our symmetrized version of the flux operator. Thus

$$C_f(t) = \mathrm{tr}[\bar{F}\ \exp(-iHt_c/\hbar)\bar{F}\ \exp(iHt_c^*/\hbar)]. \qquad \text{IIIc-11}$$

A little bit of thought shows that the result IIIc-10 is not nearly so odd as we might have first guessed. Our commutator simply gives the Heisinberg time derivative of the quantum mechanical operator h(s). h(s) is an operator which is one if you are on or past the surface s = 0. d/dt h(s) must be the flux through s = 0. We might have also guessed this if we (non-rigorously) wrote the derivative as

$$d/dt[\exp(-iHt_c/\hbar)h(s)\exp(iHt_c^*/\hbar)] =$$

$$d/dt[\exp(-\beta H/2)h(s(t))\exp(-\beta H/2)]. \qquad \text{IIIc-12}$$

In any case, we now have the rate expressed as the time integral of a flux autocorrelation function. It will turn out that this will be the form in which we apply the theory to specific problems.

One final form for the rate can be gotten directly from equation IIIc-10. We can reorder the operator by cyclic permutation under the trace to yield

$$k = (1/Q_a)\lim_{t\to\infty} \mathrm{tr}[\bar{F}\ \exp(-iHt_c/\hbar)\ h(s)\ \exp(iHt_c^*/\hbar)]. \qquad \text{IIIc-13}$$

Using our derivative formula, we can undo a derivative on the $\bar{F}$ operator. In other words

$$k = (1/Q_a)\lim_{t\to\infty} d/dt\ C_s(t) \qquad \text{IIIc-14a}$$

$$C_s(t) = tr[h(-s)exp(iHt_c^*/\hbar)h(s)exp(-iHt_c/\hbar)]. \quad \text{IIIc-14b}$$

This correlation function has the advantage of having an absolutely transparent physical interpretation. It is the correlation function which describes being on the left side of the barrier at time t = 0 and on the right side of the barrier at time t large. The rate is obviously given by the time derivative of this quantity with the appropriate normalization constant, in this case the partition function (crudely, the number of ways a reactant can exist). Before we move on to actual use of these formulae, we note a few simple facts about the nature of these functions. The method of derivation of the side-side correlation function and flux-flux correlation function from our original mixed correlation function (equation IIIc-6) makes it apparent that

$$C_f(t) = \dot{C}_{f,s}(t) = \ddot{C}_s(t). \quad \text{IIIc-15}$$

It is also easy to see that $C_f(t)$ is an even function of time (let t $\rightarrow$ -t and perform a cyclic permutation under the trace). This implies that $C_{f,s}(t)$ must be odd in t and $C_s(t)$ must be even.

d - Applications -- One Dimensional Problems

In order to test the feasibility of application of these formulae, we will first study a one dimensional problem. This problem is the rate of penetration at a given energy of the Eckhart barrier.

This is a common function used by theorists to model potentials along reaction paths. As an example, for the H + H_2 system, an extremely accurate fit to the potential along the reaction path is obtained when this quantity is fit to the two parameter Eckhart function. For details of this function, the reader is referred to Johnston's[47] book. The other main advantage to this function is that an analytic formula exists for the tunneling probability through the barrier; and so it is easy to check the accuracy of our results.

To allow application of the work of the last section, we need to put the equations into a more concrete form. This amounts to choosing a basis in which to evaluate the traces. Because we deal with a scattering problem we rigorously must use a continuum basis. Taylor[48] points out that the set of scattering states is orthogonal to the set of bound states, and together they span the Hilbert space. Calculations of Tromp[49] have shown that by using a discrete bound state basis, it is possible to mimic the behavior of the scattering Hamiltonian through the expressions of the last section. We have chosen to work directly in a scattering basis, and some experimentation has shown that the position eigenstates are the most straightforward to use. Thus in all our expressions

$$\mathrm{tr}\ O \rightarrow \int_{-\infty}^{\infty} ds \langle s|O|s\rangle. \qquad \text{IIId-1}$$

The algebra used to obtain the coordinate representations is not particularly enlightening, and so we simply list the correlation functions. We again have assumed the positive s direction to be the

direction of reaction and have placed the dividing surface at s = 0.

$$C_f(t) = (\hbar/2m)^2(\partial^2/\partial s\partial s')\left|\langle s'\left|\exp(-iHt_c/\hbar)\right|s\rangle\right|^2$$

$$-4\left|(\partial/\partial s')\langle s'\left|\exp(-iHt_c/\hbar)\right|s\rangle\right|_{s=s'=0} \qquad \text{IIId-2a}$$

$$C_s(t) = \int_{-\infty}^{0} ds \int_0^{\infty} ds' \left|\langle s'\left|\exp(-iHt_c/\hbar)\right|s\rangle\right|^2 \qquad \text{IIId-2b}$$

$$C_{f,s}(t) = (\hbar/m) \int_0^{\infty} ds' \mathrm{Im}\langle s'\left|\exp(-iHt_c/\hbar)\right|s\rangle\ \partial/\partial s$$

$$\langle s'\left|\exp(-iHt_c/\hbar)\right|s\rangle^*\Big|_{s=0}. \qquad \text{IIId-2c}$$

In equation IIId-2c Im indicates we must take the imaginary part. We also note that in equation IIId-2a, the second term will vanish if the potential is symmetric about s = 0. The way to see this is to note that if the potential is symmetric about zero, the wavefunction of the Hamiltonian in position representation will either be even or odd. In the first case the wavefunction must be zero at the origin, and in the second case, the first derivative of the wavefunction must be zero at the origin. Inserting complete sets of states of eigenfunctions of the Hamiltonian, and noting that the term is to be evaluated at s=s'=0 completes the desired demonstration. In our case, with a symmetric Eckhart barrier with the dividing surface put at s = 0 the potential is symmetric and we can ignore this term. (We will need to include this term when we move the dividing surface off the top of the barrier.) The question now is how to evaluate equations

IIId-2. All these equations are functionals of the quantity

$$\langle s' | \exp(-iHt_c/\hbar) | s \rangle . \qquad \text{IIId-3}$$

We immediately recognize this as the one dimensional Feynman propagator. The only oddity is that it has a complex value for the time coordinate given by equation IIIc-4. Feynman path integrals have been described at great length elsewhere, and we refer the interested reader to Feynman's excellent book[50]. The path integral is a functional integral over all possible paths in physical space. It forms a good deal of the basis of modern physics, but in this work we will only concern ourselves with its calculation for simple problems. For the moment, let us consider the time to be imaginary rather than complex. Purely imaginary time causes IIId-3 to be purely real. For what immediately follows this supposition is no way necessary, but it will make later discussion simpler. Because time is purely imaginary, we write the time it_c as β. We let $s' = s_n$ and $s = s_0$. If we insert the identity n-1 times into IIId-3 we obtain

$$\langle s_n | \exp(-\beta H) | s_0 \rangle = \int_{-\infty}^{\infty} ds_1 ds_2 \ldots ds_{n-1} \langle s_n | \exp(-\beta H/n) | s_{n-1} \rangle$$

$$\langle s_{n-1} | \exp(-\beta H/n) | s_{n-2} \rangle \ldots \langle s_1 | \exp(-\beta H/n) | s_0 \rangle \qquad \text{IIId-4}$$

where we have written $\exp(-\beta H)$ as

$$\Pi_n \exp(-\beta H/n). \qquad \text{IIId-5}$$

Following Feynman, let us assume we divide βH into many small pieces by letting n get very large. Another way to look at this is to imagine that the imaginary "time" increment β/n is very small. Just as if the time were real, we may assume that if the time were short enough (in other words, if n is large enough) we may assume that the potential is essentially constant over this range. We may put this to good use because an analytic form for the propagator for a system in a constant potential exists. Substituting this analytic form we may rewrite IIId-4 as

$$\int_{-\infty}^{\infty} ds_1 ds_2 \ldots ds_{n-1} \exp[(-mn/2\hbar^2\beta)\textstyle\sum_{i=1}^{n}(s_i-s_{i-1})^2]/(2\pi\hbar^2\beta n/m)^{n/2} *$$

$$\exp[(-\beta/n)\textstyle\sum_{i=1}^{n}V(s_i)]\exp[(-\beta/2n)(V(s_0)+V(s_n))]. \quad \text{IIId-6}$$

This last integral may be viewed as a functional integral equivalent of the trapezoidal rule of elementary calculus. As the number of divisions gets large, IIId-6 becomes exact. Thus we see that in order to evaluate the propagator the task is to evaluate a many dimensional integral. The order of this integral is bound to be very large, and so we now develop a way to deal with these kinds of problems. We first note that formal extensions of something like Simpson's rule are not at all the way to go. These methods become prohibitively slow for anything over two or three dimensions, and are totally hopeless for twenty or thirty dimensions. The method of choice to solve this type of problem is known as Monte Carlo integration. In its simplest

form, one guesses a value for the coordinates in the range of integration. The integrand is then evaluated at this point. This process is repeated many times, and all of the points are then added. Division by normalization equal to the number of points yields the desired approximation to the integral. We will perform a number of transformations to equation IIId-6 to make it more amenable to this type of approach. We initially note that the first factor in IIId-6 is simply a Gaussian. Since we know how to do these kinds of integrals, it would be nice if we could treat this part of the problem exactly. To do a Monte Carlo integral it is also desireable to have the variables of integration run over a slightly more tractable range than $(-\infty,\infty)$. Let us define a set of variables $\{z_k\}$ such that

$$\langle s_n|\exp(-\beta H)|s_0\rangle = \int_0^1 dz_1 \int_0^1 dz_2 \ldots \int_0^1 dz_{n-1}\ C\exp[(-\beta/n)\textstyle\sum_{i=1}^{n} V(s_i)] \ *$$

$$\exp[(-\beta/2n)(V(s_0)+V(s_n))]. \qquad \text{IIId-7}$$

The constant C is given by

$$C = \int_{-\infty}^{\infty} ds_1 ds_2 \ldots ds_{n-1}\ \exp[(-mn/2\hbar^2\beta)\textstyle\sum_{i=1}^{n}(s_i-s_{i-1})^2]/$$

$$(2\pi\hbar^2\beta n/m)^{n/2}. \qquad \text{IIId-8}$$

To see that this is true, consider a two dimensional integral

$$\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \; w(x_1,x_2)F(x_1,x_2). \qquad \text{IIId-9}$$

We define a z_2 variable such that

$$dx_2 w(x_1,x_2) = c(x_1)dz_2 \qquad \text{IIId-10}$$

which implies $\int_{-\infty}^{x_2} dx_2' w(x_1,x_2') = c(x_1)z_2.$ IIId-11

We require that when $x_2 \to \infty$, $z_2 \to 1$ so

$$c(x_1) = \int_{-\infty}^{\infty} dx_2' w(x_1,x_2'). \qquad \text{IIId-12}$$

By similar logic we find

$$C = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx_1 dx_2 w(x_1,x_2). \qquad \text{IIId-13}$$

Now IIId-8 is just the integral over a set of intermediate points of the free particle propagator. Thus

$$C = \langle s_n | \exp(-\beta H_o) | s_0 \rangle = \exp[(-m/2\hbar^2\beta)(s_n - s_{0-1})^2]/(2\pi\hbar^2\beta/m)^{1/2} \qquad \text{IIId-14}$$

What remains is to express the $\{s_k\}$ as functions of the $\{z_k\}$. Then the prescription is to choose the $\{z_k\}$ between 0 and 1 in order to generate the values of $\{s_k\}$ and hence the values of the integrand. The notion here is to proceed sequentially with an equation like IIId-11. Thus

$$z_1 = \int_{-\infty}^{s_1} ds_1' \int_{-\infty}^{\infty} ds_2' \ldots ds_{n-1}' w(s_1', s_2', \ldots, s_{n-1}')/$$

$$\int_{-\infty}^{\infty} ds_1' ds_2' \ldots ds_{n-1}' \; w(s_1', s_2', \ldots, s_{n-1}'). \quad \text{IIId-15}$$

A bit of algebra yields

$$z_1 = (n/n-1)^{1/2} \exp[(-m/2\hbar^2\beta)(s_n - s_0)^2]/(2\pi\hbar^2\beta/mn)^{1/2} *$$

$$\int_{-\infty}^{s_1} \exp[(-mn/2\hbar^2)((s_n - s_1')^2/(n-1) + (s_1' - s_0))] ds'. \quad \text{IIId-16}$$

It is possible but tedious to derive a formula for the general term z_k. This term, like the term for z_1, will be composed of a constant factor times an integral over the corresponding variable s_k. The crucial point is that we can perform a change of variables which absorbs the factor in front of the integral to yield

$$z_k = \int_{-\infty}^{F(s_k)} dy \; \exp(-\pi y^2) \quad \text{IIId-17a}$$

where

$$F = [(mn/2\pi\hbar^2\beta)((n-k+1)/(n-k))]^{1/2}$$

$$(s_k - (s_n + (n-k)s_{k-1})/n-k+1). \quad \text{IIId-17b}$$

At this point we're almost there. We simply need to invert IIId-17b. We do it now on paper:

$$s_k = ((n-k)/(n-k+1))s_{k-1} + s_n/(n-k+1) +$$

$$[(2\pi\hbar^2\beta/(mn))*(n-k)/(n-k+1)]^{1/2}\,Em(z_k). \quad \text{IIId-18}$$

$Em(z_k)$ is the inverse of the integral in IIId-17b, and it turns out that there are good analytic approximations to it[52]. Our method of solution of IIId-3 is now complete. We choose a set of numbers $\{z_k\}$. These numbers, between zero and one, sequentially generate the variables $\{s_k\}$. This process is then repeated many times in order to generate the Monte Carlo integral. One should approach the exact number as both the number of Monte Carlo passes and the divisions of the path integral, n, are increased. A bit later we discuss how large these numbers actually seem to be.

Now that we have a method to evaluate the propagator, it would seem that we have the answer to our problem. In order to evaluate, for example, $C_f(t)$ we need to compute the propagator for different values of s and s' about the origin, and then use this data to numerically compute the second derivative in IIId-2a. (Recall that because the potential is symmetric, the second term vanishes.) This is done at many values of the real time for a given value of β , and the integral of these numbers gives the rate. This seems like a good idea, and as a matter of fact, it was tried. Results were very poor, and this is certainly due to the fact that we work with a complex value of the time. In equation IIId-18 we need to replace β by $(\beta/2-it/\hbar)$. The immediate effect of this is to cause the coordinates generated to become complex. We then take the potential at complex

values of the coordinate, and exponentiate that. One might expect poor numerical behavior, and one would be correct in that expectation. The Eckhart potential, which is perfectly well behaved on the real line, has poles in the complex plane, and though all the equations derived are formally correct, there is no good way to implement them directly on a computer.

The only way around this difficulty that we could find was to use our ability to calculate these quantities on the real line. If an analytic function defined on the complex plane is known exactly on the real axis, then it is known everywhere. We, of course, don't know the analytic form for the function, but we can take the data we obtain on the real line, and fit it to an analytic function. This function can then be continued into the complex plane to obtain the desired result. Numerical analytic continuation is a tool which has come to the aid of scattering theorists a few times in the past. Miller, et. al.[53], have used this method to continue classical trajectories into the complex plane to obtain semiclassical tunneling probabilities. Schlessinger[54] has studied scattering matrix elements with this approach. Before the method is described, we list some of its drawbacks. The first and most obvious one is that you are in no way assured of getting the right answer. Data on the real line may not accurately convey complicated information about the pole structure in the complex plane. It is our hope that this will not be too severe a problem, because in our one dimensional case we have, at least approximately, the exact analytic behavior. Putting all our formulae together in one place we have

$$\langle s_n|\exp(-\beta H)|s_0\rangle = \exp[(-m/2\hbar^2\beta)(s_n-s_0)^2]/(2\pi\hbar^2\beta/m)^{1/2} *$$

$$\int_0^1 dz_1 dz_2 \ldots dz_{n-1} \exp[(-\beta/2n)(V(s_0)+V(s_n))]$$

$$\exp[(-\beta/n)\textstyle\sum_{i=1}^{n} V(s_i)]. \qquad \text{IIId-19}$$

The prefactor in this last equation is the free particle propagator. If the analytic structure of the total propagator does not vary vastly from this, we should have no problem.

The second problem is related to the first. Any data we obtain on the real line are not going to be exact. (No numerical calculation is.) In the Monte Carlo calculation we perform, there is bound to be some noise. Comparison of numerical results to exact results for the simple harmonic oscillator suggests that one can hope for errors no less than three to five percent. The question is, how errors of three to five percent will translate in the analytic continuation. Close to the real line we expect to experience no difficulties, but as we go farther away (i.e., as the time gets large) errors will certainly build in. We now return to the statement made at the beginning of this chapter. By formulating this theory along the lines of transition state theory, we hope not to need to follow the dynamics for a very long time. In terms of the correlation function $C_f(t)$, we hope that it falls to zero very quickly. It is hoped that a judicious choice of the dividing surface will increase the efficiency of the calculation. If one really wanted to do this right, the dividing surface could be chosen as a periodic orbit on the surface following

the elegant work of Pollak and Pechukas[55]. All these matters will be studied in depth when we get to actual application to the Eckhart barrier.

The function we use to fit the data is a continued fraction. Schlessinger[54] has extensively studied the properties of these functions; so we will simply list the appropriate formulae. If we have n+1 data points we fit to a function

$$C_n(s) = f(x)/(1 + (a_1(x-x_1)/(1 + a_2(x-x_2)/\ldots$$

$$\ldots\ldots(1 + a_n(x-x_n)))\ldots). \qquad \text{IIId-20}$$

This can be inverted to give the a_n's in terms of another continued fraction

$$a_n = (1/(x_n-x_{n+1}))\{1 +(a_{n-1}(x_{n+1}-x_{n-1})/(1 + (a_{n-2}(x_{n+1}-x_{n-2})/$$

$$\ldots\ldots\ldots/(1 + a_1(x_{n+1}-x_1))/(1-(f(x_1)/f(x_{n+1}))\} \qquad \text{IIId-21}$$

and $a_1 = \{f(x_1)/f(x_2)-1\}/(x_2-x_1)$. IIId-22

This method of analytic continuation was used to continue the Feynman propagators. One simply substitutes complex values of x in equation IIId-20. We remember $t_c = t-i\hbar\beta/2$, and so we calculated values of the propagator on the real line about the value $\hbar\beta/2$. We seemed to need about ten to fifteen data points for an accurate analytic

continuation. For each data point, we found it necessary to break up the Feynman path integral into about twenty steps - in other words we had to perform a twenty dimensional integral. This in turn required about 1000 Monte Carlo passes to converge. The functional form for the Eckhart barrier may be written as

$$V(s) = V_o \mathrm{sech}^2(s/a). \qquad \text{IIId-23}$$

Johnston lists results in terms of a tunneling factor Γ which is given by

$$kQ_a = \Gamma(1/(\hbar\beta))\exp(-\beta V_o). \qquad \text{IIId-24}$$

The two dimensionless parameters which characterize the potential are

$$\alpha = \pi(2mV_o a^2/\hbar^2)^{1/2} \qquad \text{IIId-25a}$$

$$u = \hbar\beta(2V_o/(a^2 m))^{1/2}. \qquad \text{IIId-25b}$$

Table I lists results obtained for a few values of these parameters. A large Γ implies large quantum effects. We see our results are quite accurate. Figure IV gives $C_f(t)$ for the specific case of $\alpha = 12$ and $u=8$ ($\Gamma = 22$). It is a well behaved function, and it does in fact decay quickly to zero. It is essentially zero in about half the harmonic period of the barrier. (By harmonic period we simply mean the absolute value of the period which would be obtained from the inverted barrier.) This rapid decay is not surprising, because for a

one dimensional problem, transition state theory is classically exact if one places the dividing surface at the top of the barrier. This is because recrossing of the barrier is not possible. The time frame is set solely by the time of quantum mechanical tunneling, which is bound to be very fast. A more difficult problem is encountered if the transition state theory is not exact. In a one dimensional problem, barrier recrossing will be created by moving the dividing surface off the top of the barrier into the reactant region. This indeed made the problem more difficult, and we could not obtain converged results. Figure V shows one such attempt. The function $C_f(t)$ behaves as we might expect. At $t = 0$ it is larger than its counterpart with the dividing surface at $s = 0$. This must be due to the fact that in the reactant region, initial flux must be greater due to the lower value of the potential. As time progresses, some of the flux bounces off the top of the barrier, and the correlation function can become negative. This lack of sucess for the shifted barrier does not bode well for future numerical application of the theory in the manner discussed. In general, we hope this method would succeed when transition state theory will be a very good approximation to the classical rate, so that we don't have to analytically continue our results very far into the complex plane. We expect that it will also be the case that the structure of the complex propagator will be easier to mimic.

We here briefly mention a calculation that was undertaken to try to employ these approaches in more than one dimension. We studied the collinear $H + H_2$ reaction. Results could not be accurately obtained

for this problem. The reason for this is certainly many-fold, but it was certainly not due to barrier recrossing phenomena. (At moderate energies transition state theory is well known to be classically exact or at least very accurate for the $H + H_2$ problem.) We choose to use a cartesian coordinate system to avoid the ambiguities mentioned earlier with curvilinear coordinate systems. One of many problems encountered involved traces over coordinate variables which would allow one to stray into non-physical regions of the potential energy surface. Another problem encountered is that while there were no barrier recrossings, the dynamics are simply not as rapidly completed as in the one dimensional case. Correlation functions were found which "lived" an order of magnitude longer than the one dimensional case. It is possible that a massive effort of methods of calculation (such as has gone into the calculation of quantum mechanical potential energy surfaces) could solve many of these problems, but it is not clear how long this might take, and if it would finally yield the desired results.

These results tend to lead us to rethink our initial goals for this research. It is probably not useful to think of this formal structure mainly as a tool for calculation. A new method for the calculation of the propagators in complex time, without the need for analytic continuation, would be necessary for any future calculation. These formulae can rather stand as a tool for analytic study of Boltzman rate constants, either in their exact quantum form, or in various approximations to them such as transition state like approaches. A very important subject of inquiry might be to study the

effect of external interactions (i.e., not part of the Born-Oppenheimer potential energy surface) on the rate constants of chemical reactions.

IV - Frequency Variation Along a Reaction Path

a - Introduction

We have seen in chapter two of this thesis, the frequency variation along a reaction path can have a profound effect on the physics of chemical processes. One way to look at the results of chapter II is that all rotationally inelastic effects in the three dimensional reaction $H + H_2$ are due to variations in the frequency of the bend modes along the reaction path. Perhaps this interpretation is a bit extreme, but the hindered rotors are closely approximated by harmonic oscillators of variable frequency in the interaction region. We tend to always think of these types of problems in terms of classical pictures. One visualizes an oscillator moving physically along a reaction path, and the rate of vibration of this oscillator changes as the motion along the reaction path progresses. Quantum mechanically we know that this intrepretation is not valid. To maintain a physical picture, one might think of a wavepacket evolving on the potential energy surface. At a given instant, we of course know that we cannot say with infinite accuracy where on the surface we are, because the uncertainty principle requires that the wavepacket has a spread in probability density. If we freeze time, the most we can say is that a continuum of positions along the reaction path are possible, and they are all weighted by a probability density.

At this point we ask what this does to our conception of the

variable frequency oscillator? If at a given instant, a continuum of positions along the reaction path are possible, then a continuum of values for the frequency are also possible. Each frequency will be weighted by the probability density of the point along the reaction path. One way to describe the situation is to consider the oscillator degree of freedom to be represented by a field. This field will have a density of states given by the density of the s coordinate. We realize that this probability density will also be a function of the time in a scattering problem. This view of frequency variation is what motivates the present chapter. We introduce a simple model which will allow us to treat the quantum mechanical probability spread inherent in a wavepacket. For ease of application we will specialize to a bound state system, in other words, a system in which the density of states of the variable frequency oscillator is constant in time. This density of states will then only be a function of the one of the degrees of freedom.

This section will certainly be much more speculative than the preceeding two, and thereby a less complete, self-contained, formal structure. The model does yield excellent results and could be a good starting point for future research. In what follows, we specialize to two dimensions, but we will make clear how one might extend the theory to higher dimensionality.

b - Theoretical Method

Let us suppose that we can write the total Hamiltonian as

$$H = P_s^2/2 + P_q^2/2 + \tfrac{1}{2}(\omega(s) + \omega_o)^2 q^2 + V_o(s) + f(s)F(q). \quad \text{IVb-1}$$

We explicitly include a direct coupling between the degrees of freedom in the last term. If at a given time the direct coupling is very weak, and the variation in frequency does not vastly effect the motion in the s degree of freedom, then the distribution in frequencies is given by

$$P(\omega(s)) = |\phi(s)|^2 \quad \text{IVb-2}$$

where $\phi(s)$ is the wavefunction for s motion in the absence of q. In other words

$$(P_s^2/2 + V_o(s))\ \phi_n(s) = E_n\ \phi_n(s). \quad \text{IVb-3}$$

It is useful to first examine the case where $f(s) = 0$. The present simple model implies that to get the shift in ground state energy, we simply have to average the energy over the s degree of freedom. In other words

$$\Delta E_{gs} = \tfrac{1}{2} \int ds\ \phi(s)^2 \omega(s). \quad \text{IVb-4}$$

This is nothing startling; it is simply the first correction to the Born-Oppenheimer energy. Of course this is not the exact answer, because we neglect indirect coupling which formed the basis of chapter II.

We are here more interested in the case in which there is a direct coupling. In order to study this, we will once again make use of the machinery of Feynman path integrals[56]. The nature of our system is totally described by the Feynman propagator

$$K(s_1,s_2;q_1,q_2) = \langle s_2 q_2 | \exp(-iHt/\hbar) | s_1 q_1 \rangle. \qquad \text{IVb-5}$$

We consider performing the path integral over the q degree of freedom with the variation of $\omega(s)$ suppressed. To make the problem possible to solve analytically, we suppose that the coupling is linear in q. With these two assumptions the path integral over q is given by the propagator for a forced harmonic oscillator. Because we do not suppress the variation of f(s) for the q degree of freedom, s can be thought of as a time variable. Thus, a full forced oscillator kernel must be used. The variation in frequency as a function of s is assumed to be slow enough so that the dependence of frequency on s may be treated parametrically. This corresponds exactly to our original statement that the s wavefunction density gives a distribution of frequencies for q. Formally, this means we approximate the propagator as

$$K(s_1,s_2;q_1,q_2) = \int D[s] \int ds' P(s') K_{s'}(q_1 q_2 t)$$

$$\exp((i/\hbar) \int_{s_1}^{s_2} L_s dt). \qquad \text{IVb-6}$$

Here L_s is the Lagrangian for motion in the $V_o(s)$ potential alone.

The structure of the model is such that the problem is exactly analogous to the problem of a particle (the s degree of freedom) interacting with a field.

c - Application

We test the model on the simplest problem available: that of two coupled oscillators.

$$H = P_s^2/2 + P_q^2/2 + \tfrac{1}{2}(\omega(s) + \omega_o)^2 q^2 + \omega_s^2 s^2 + f(s)q \qquad \text{IVc-1a}$$

$$\omega(s) = s^2(.008/250) \qquad \omega_o = .0087 \qquad \text{IVc-1b}$$

$$f(s) = C \times 10^{-5} s^2/250 \qquad \text{IVc-1c}$$

$$\omega_s = .02 \qquad \text{IVc-1d}$$

All parameters are given in atomic units; so $\hbar = 1$. The question of physical pertinence in this bound state problem is the effect of coupling between the modes on the energy levels. If we first consider the case where C = 0, then IVb-4 gives for the shift 4.0×10^{-4} a.u. Simple second order perturbation theory gives a value of $\Delta E_{gs} = 4.55 \times 10^{-4}$ a.u. Calculation of the exact shift shows it to be 4.12×10^{-4} a.u. We do a bit better with the Born-Oppenehimer correction, and this must be due to the fact that we take the variation of frequency into account to infinite order, at least in some approximate fashion.

For a more rigorous test we now study the case where direct coupling is also present. Again we emphasize that by construction of the model, the problem is exactly analogous to that which gives rise to the Lamb shift[57] in electromagnetic theory. The new interpretation in our physical problem is that the emission and subsequent reabsorption of virtual phonons rather than photons results in a shift in the energy levels. It is perhaps difficult to see this as a more perspicuous physical model than a simple classical one, but we feel it is certainly more closely alligned with the problem. If we are interested in the shift caused to the ground state of both oscillators, we must first express the field oscillator kernel ($K_s'(q_1,q_2)$) of equation IVb-6 in a harmonic basis, and then calculate the effect of this coupling. This involves a fair amount of difficult algebra, but because the problem is in direct analogy to the interaction of the electromagnetic field with matter, we may take previous existing results almost exactly. Feynman[50] has calculated a general formula for the harmonic matrix elements of a forced oscillator kernel. This he has used to calculate the effects of the interaction just mentioned. This calculation, of course, just results in the well known type result:

$$\Delta E_{gs} = \sum_n \int ds \left|\langle 0|f(s)|n\rangle\right|^2 PP(E_0-E_n-\hbar\omega(s))^{-1}(1/(2\omega(s)))P(s). \quad \text{IVc-2}$$

Here PP indicates the Cauchy principle part. Because of the form we choose for f(s), only n=0 and n=2 are admitted in the sum over states. P(s) is the density we choose for the field of the adiabatic

oscillator. At this point one has to admit that the model is not complete. As of yet, we have not been able to derive a uniform, rigorous method of choice for this function. We are now forced to make our choice on logical physical grounds alone. This would certainly be an area for future work. What one would like is to choose the function which is guaranteed to give the best result. Some attempts at the derivation of a variational principle have been made. Like so many variational problems, all we have been able to see are possible first variational approaches. In other words we have no true maximum principle. If this type of method is ever to become useful some rigorous approach will have to be developed. It is still our feeling that some kind of variational principle must provide the answer.

In any case, in order to see if the model has any validity, we make a guess at this probability density. We realize that the shifts we are interested in studying may be thought to come about because the simple harmonic oscillator energy levels are not the true eigenstates of the full Hamiltonian. Due to the choice of our coupling the shifts arise from mixings of the zeroth and second vibrational states of the s degree of freedom. (This is in exact analogy to the problem considered in chapter two, in which the couplings were also due to inexact choices of eigenfunctions. This is perhaps not too terribly useful to note, because all problems in quantum mechanics boil down to this exact problem.) Thus we make as a natural choice for the density the average of the unperturbed, zeroth order states:

$$P(s) = (|\phi_0(s)|^2 + |\phi_2(s)|^2)/2. \qquad \text{IVc-3}$$

The effects we are interested in are very small, so we plot in figure V the energy shift due to the direct coupling alone. (In other words, the difference between the result for $C = 0$ and for $C \neq 0$.) We plot along with our field model the second order perturbative results (perturbative in both the frequency variation and the coupling), and the exact results obtained from diagonalization of the Hamiltonian matrix. The comparison to simple perturbation theory is quite striking. We treat the direct coupling perturbatively, but because we treat the frequency variation to infinite order in an approximate manner the accuracy of the model is much higher than simple perturbation theory. We might at this point ask how crucial the choice we made for P(s) was. The answer is that while other logical choices (such as $|\phi_0(s)|^2$ alone) give slightly different answers, the results are still quite good, and in all cases tested, a lot better than the perturbation theory.

d - Remarks

In a simple test case this model for variable frequency quantum mechanical oscillators has been shown to be very accurate. For a many dimensional problem, the theory might also be applied. For degrees of freedom which, to a good approximation interact only with each other, one just couples phonon fields one by one to the reaction coordinate. For strongly interacting degrees of freedom field-field effects must

be included in the propogator. (In this case things get very hard, and perhaps this model would be more trouble than it is worth.)

For the strong coupling regime, where one could not derive equation IVc-2 making use of the perturbation theory, one might be able to gain insight into scattering data using techniques now commonly used for field interactions which are much stronger than the electromagnetic field-matter interaction (which goes as 1/137, or the fine structure constant.) In any case the first order of business would be to derive a rigorous method for choice of the density of states.

V - Conclusion

This thesis has been concerned with calculational tools and the interpretations they might provide the theoretical chemist. We feel it is crucial to stress the interpretive aspect of theoretical chemistry. The ability to do complex calculations on modern high speed computers has at times obscured the goal of any physical science, which must be to gain a greater understanding of general principles. Too often it seems that calculations are looked upon as ends in themselves, rather than useful tools to garner greater understanding of chemical processes. The way to proceed to discovery of physical insight is, of course, up to the individual investigator, and totally a matter of intellectual taste; and calculation is certainly a crucial tool.

A final admonition is left for the theoretical chemist. One must not be afraid to be wrong, at least quantitatively in the application of new ideas. So much has been made possible by accurate quantum chemical calculations of potential energy surfaces for small systems, that we have become paralyzed in the field of chemical dynamics. Distress at three significant figure accuracy has at times superceded desire for order of magnitude understanding. It is our feeling that if further progress is to be made in the subject, investigators will have to concede defeat, at least momentarily, in "exact" calculations for most systems. General understanding of larger problems must be the focus.

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FIGURE CAPTIONS

Figure I - The coupling elements $B_{2,1}(s)$ and $B_{3,3}(s)$ as a function of reaction coordinate

Figure II - Solid line is the system - bath prediction for the bend transition $(n_2,n_3,n_4) = (0,0,0) \rightarrow (0,0,2)$ times 4. The point is the result of Schatz and Kuppermann (ref. 10) for the sum of the $j = 0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$.

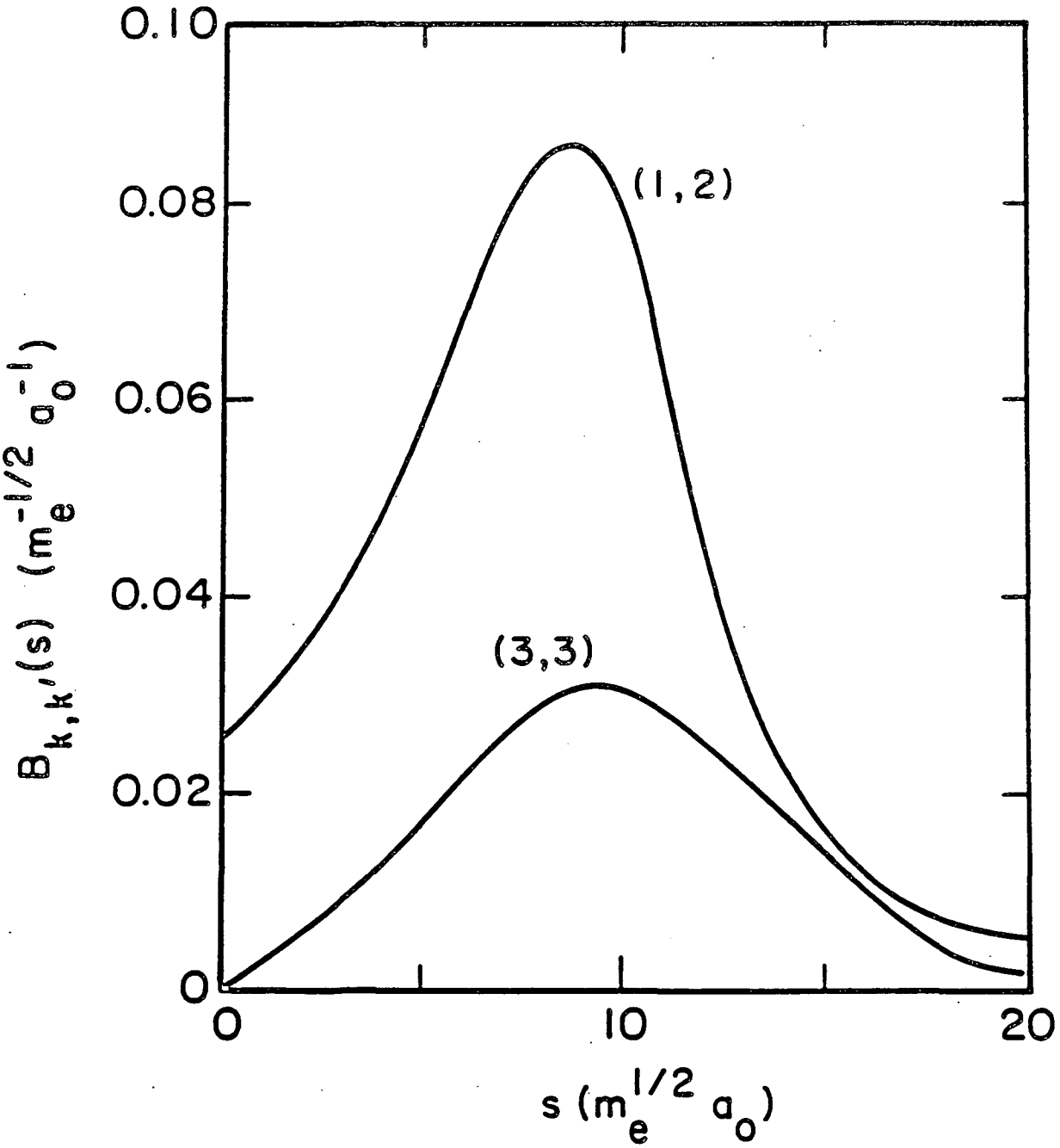
Figure III - A sample two dimensional energy surface with dividing surface at $R = R_o$.

Figure IV - The flux-flux autocorrelation function for the Eckhart potential with $\alpha = 12$ and $u = 8$ ($\Gamma = 22$).

Figure V - The solid line is the flux-flux auto correlation function for the dividing surface at $s = 0$, the dashed line is for $s = .1$. The actual value of Γ is 4.54.

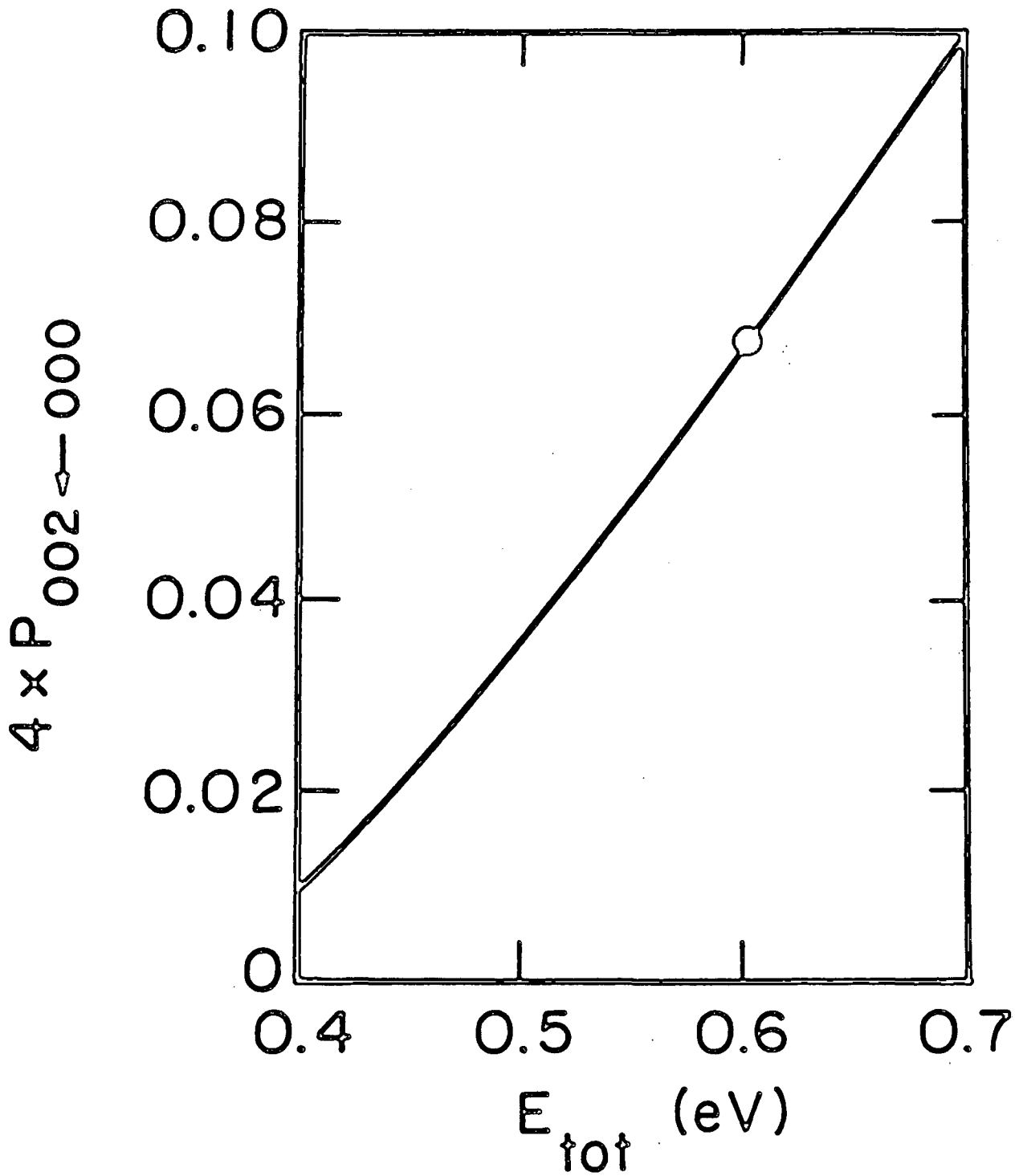
Figure VI - The line gives exact quantum results, the circles the present model's results, and the triangles the second order perturbative results.

FIGURE I



XBL 833-8617

FIGURE II



XBL 833-8616

FIGURE III

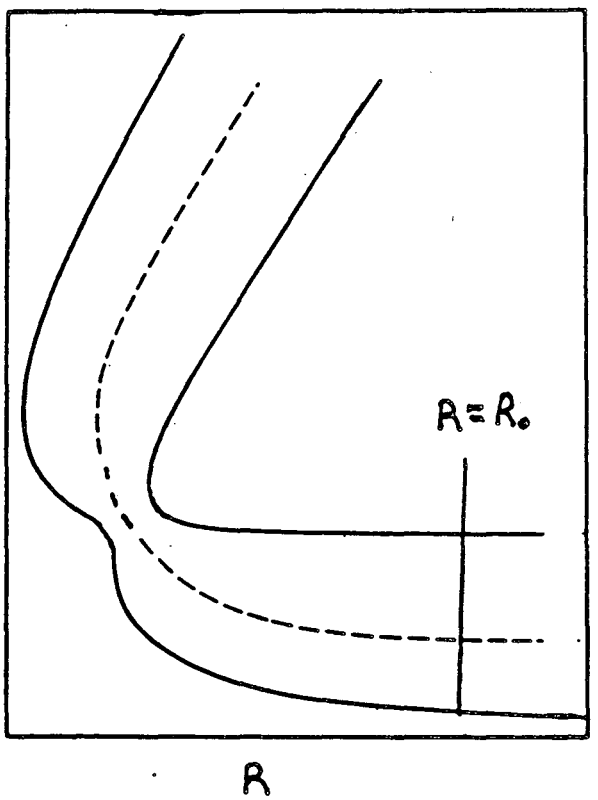


FIGURE IV

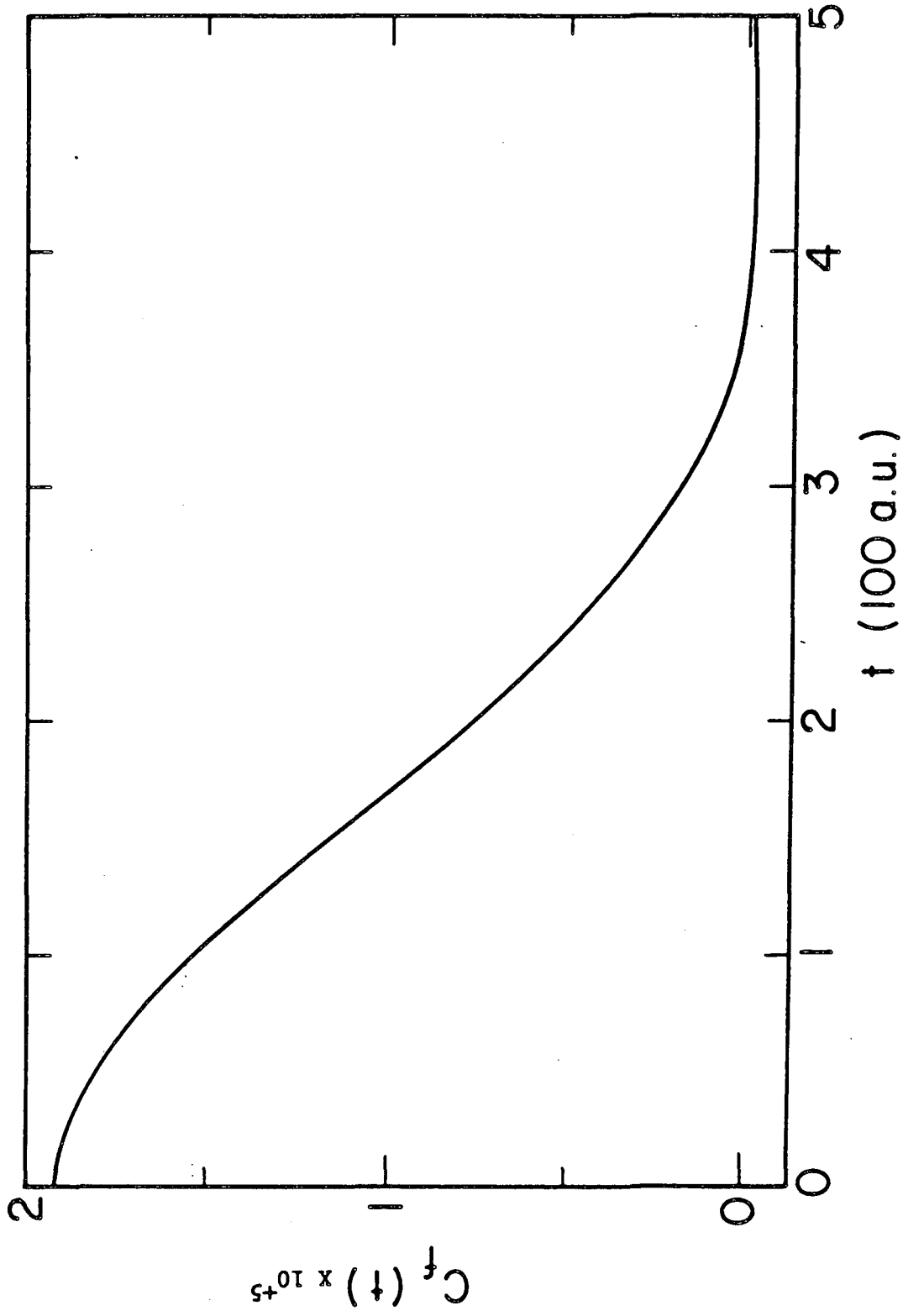


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FIGURE V

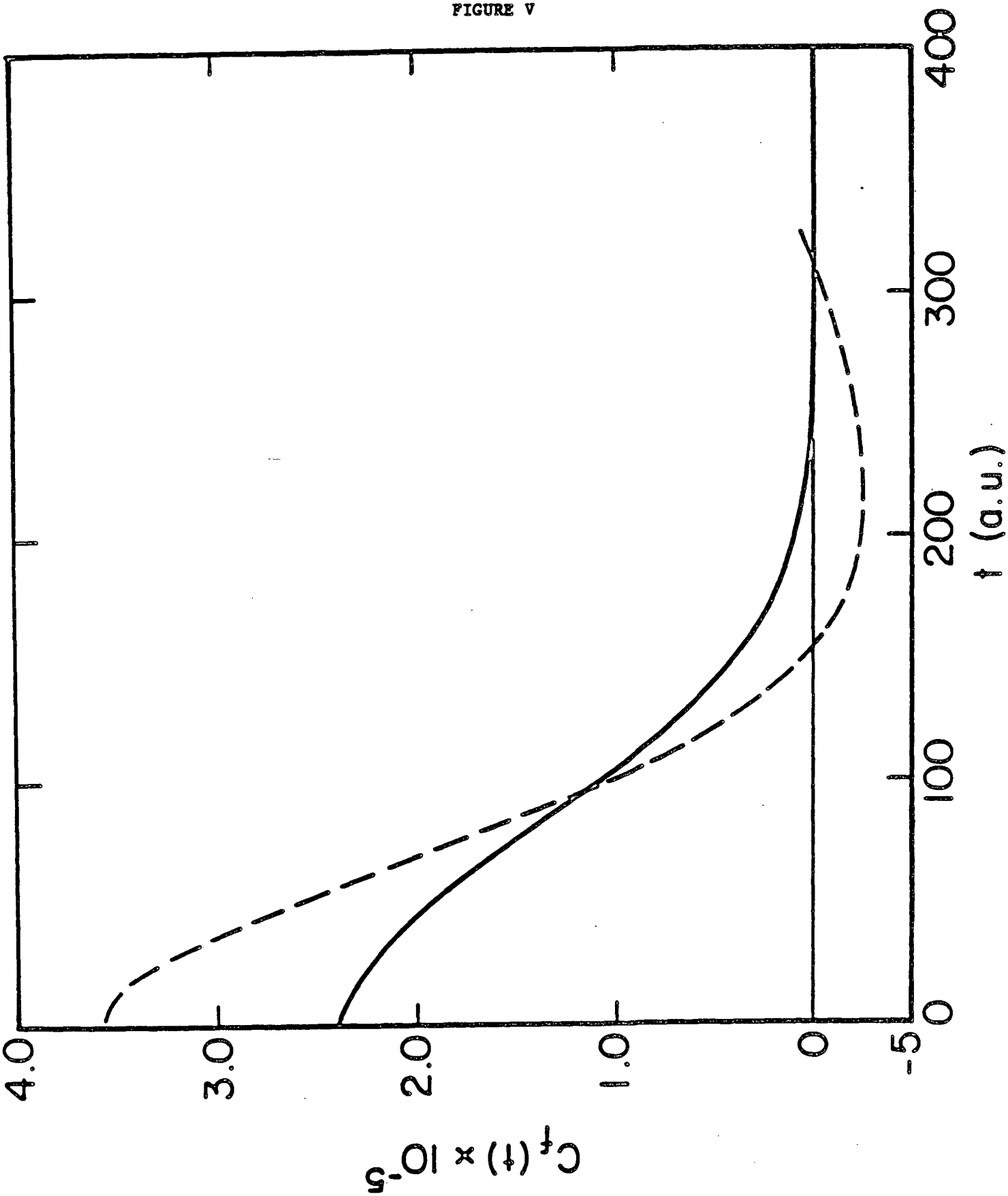
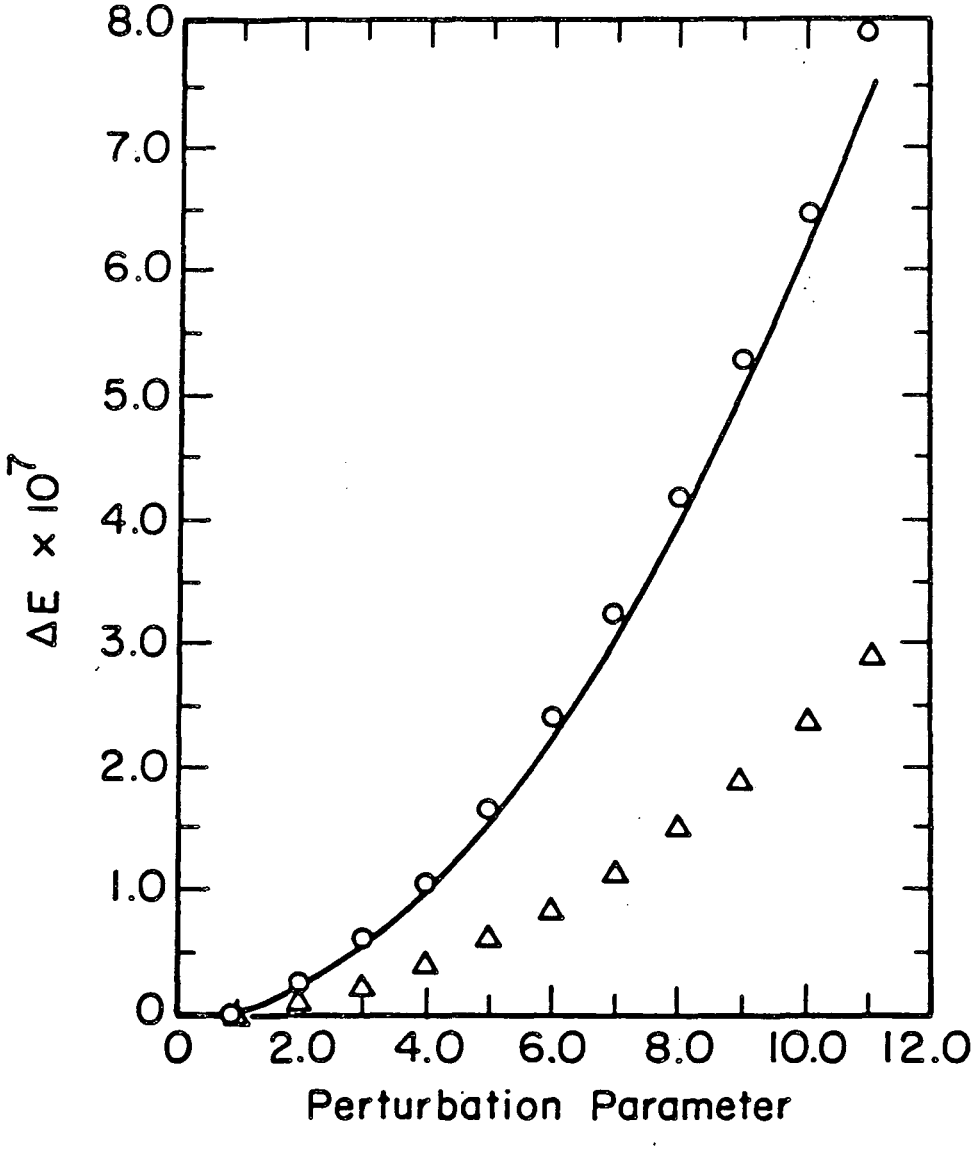


FIGURE VI



XBL 837-10727

TABLE I

$\alpha = 12$ for all cases

u	Johnston[47]	Present
2	1.2	1.21
4	2.1	2.13
8	22.0	22.3
10	162.0	163.1

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