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LINEAR $H + H_2$: EXACT AND APPROXIMATE REACTION PROBABILITIES

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1. INTRODUCTION

Most of the work described in this talk was performed in collaboration with Donald G. Truhlar and was part of his Ph.D. doctoral thesis at Caltech. This work is continuing with the collaboration of John Q. Adams and Joel Bowman. A preliminary report of a small part of this talk has already appeared¹ and another paper² is presently in press. Additional parts of this talk will be submitted for publication in the Journal of Chemical Physics in the near future.

The theoretical investigation of reactive collisions between hydrogen atoms and hydrogen molecules in their various isotopic combinations is probably the most extensive one performed on reactive systems. The obvious reason is that the system is one of the simplest conceivable ones and is therefore the most susceptible to a theoretical attack. Restriction to collinearity is dictated by mathematic convenience and is chemically justified on the basis that the linear configuration of

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the ground electronic state of H_3 is the most stable one. However, quite apart from this justification the performance of calculations on a one-dimensional physical world is justifiable because exact quantum mechanical calculations for this system can be performed and can be used for testing the validity of classical and other approximate calculations for the same model system, as well as for testing theories of reaction rates such as transition state theory. For example, the physical idea behind the latter should be as valid for this one physical dimensional world model as for the real three physical dimensional world.

2. PAST WORK

The calculation of reaction probabilities in collinear collisions between H and H_2 is a two-mathematical-dimension (2-MD) problem in center of mass coordinates. Because of the difficulties of solving the Schrödinger equation for such a system using realistic potentials, most past work has been devoted to the investigation of simplified potential surfaces. In 1944 Eyring, Walter and Kimball³ investigated an L shaped infinitely deep rectangular well. In 1959 Mazur and Rubin⁴ investigated the scattering of a wave packet by a similar well. In 1962 Mortensen and Pitzer⁵ did some preliminary calculations with a more realistic London-Eyring-Polanyi-Sato surface. These calculations were extended in 1968 by Mortensen⁶ and constituted the most realistic model calculations of this system done prior to the work

reported here. In 1967 Diestler and McKoy⁷ developed a convenient boundary value method for solving the two-mathematical dimension Schrödinger equation and applied it in a restricted manner to L shaped rectangular well and parabolic well potentials. In 1969 Tang, Kleinman and Karplus⁸ investigated an L shaped rectangular well with a raised platform in the corner of the L to mimic the activation barrier. Finally, in 1969 Wyatt⁹ scattered a wave packet off the Shavitt, Stevens, Minn and Karplus (SSMK) scaled surface¹⁰ at a single incident energy. This list represents all of the exact quantum mechanical calculations reported so far for collinear $\text{H} + \text{H}_2$ reactive collisions using model potential energy surfaces.

The calculations summarized below differ from the ones above in that, in addition to using a realistic potential energy surface, they scan a wider range of incident translational energies and include an investigation of the effect of reagent vibrational energy on the reaction probabilities as well as the partitioning of the total energy of the system among translational and internal degrees of freedom of the products.

3. POTENTIAL ENERGY SURFACE

As in all of the calculations described above, the collisions were considered to be electronically adiabatic and to occur on the ground electronic surface. We fitted the scaled SSMK surface¹⁰ according to a method described by Wall and Porter.¹¹ The fit was very good

both in the strong interaction region around the transition state as well as for the separated reagent and separated product regions. The fitted surface was made to fall off more rapidly than the scaled SSMK one as the separation between the reagents and between the products increased. The purpose of this requirement was to save computer time. It is believed that this surface is, nevertheless, representative of the H_3 system. Since the spirit of the calculation is to obtain accurate quantum mechanical results against which approximate calculations and theories can be tested, it is only important that the shape of the surface be representative rather than it be an accurate duplicate of the correct H_3 one.

4. NUMERICAL METHOD

The method used was a slight variation of the Diestler and McKoy boundary value method.⁷ The one mathematical dimensional wavefunctions for the bound states of the reagents and the products were used as part of the value of the wavefunctions along the boundaries. They were obtained numerically by a one-dimensional counterpart of the boundary value method. In addition, the resulting linearly independent solutions of the 2-MD Schrödinger equation obtained were subjected to an R matrix analysis. The calculation was done at several grid sizes and extrapolated to an infinitely fine grid. The extrapolated R matrix was very nearly symmetrical. It was then symmetrized, and from it the S matrix and the transition probabilities were calculated. The latter are accurate to about 1%.

5. RESULTS AND DISCUSSION FOR LOW ENERGIES

We consider first the case in which the reagent molecule is in its ground vibrational state and in which the relative translational energy E_0 between the reagents is insufficient to produce vibrationally excited products. Figure 1 shows the dependence of the reaction probability on E_0 for these exact 2-MD calculations, as well as those of two approximate 1-MD models. In one of them, the conservation of vibrational energy (CVE) model, the potential barrier is taken as the potential energy curve along the reaction coordinate and the motion along this coordinate is assumed to be separable from the transverse motion. This implies that the energy in this transverse motion is constant along the reaction path and therefore that the quantum number of this transverse motion varies. In the other one, the vibrationally adiabatic (VA) model, it is also assumed that motion along the reaction coordinate is separable from motion transverse to it. However, it is further assumed that the quantum number of this transverse motion is conserved as the system evolves from the reagent region through the transition state to the product region. Since the curvature of the potential energy surface in the transverse direction is less in the transition state region than in either the reagent or the product region, this assumption requires that there be interconversion between energy in the transverse mode and energy along the reactive coordinate. This interconversion is represented by modifying the CVE 1-MD barrier as follows. At each point along the reaction path we add to the CVE

potential the zero point energy of the transverse mode. The resulting 1-MD VA barrier as well as the CVE one are shown in Figure 2. As can be seen, the height of the VA barrier with respect to the separated reagents is smaller than that of the CVE one by about 3 kcal/mole. In addition, the VA barrier is much broader than the CVE one in the transition state region. From Figure 1 it can be seen that the VA model is a better approximation to the exact 2-MD results both in absolute value and in shape. The 2-MD reaction probability curve permits a calculation of the exact reaction rate constant for collinear $H + H_2$ on the present surface. It is also possible to calculate the transition state rate constant for the same collinear reaction. Such calculations are underway and should be very useful in testing the validity of the dynamical assumptions underlying transition state theory.

6. RESULTS AND DISCUSSION FOR HIGH ENERGIES

Figures 3 and 4 depict the variation of reaction probabilities of the ground vibrational state of H_2 with either the total or the translational energy of the reagents. At the highest energy used, the ground and first two excited vibrational states of the products are accessible. It can be seen that these curves show an oscillatory behavior which is generally associated with the opening of exit channels as the energy increases. It is interesting to note that as the first vibrationally excited state channel of both reactive and non-reactive collisions open, the total reaction probability

decreases, whereas the probability of elastic collisions (not indicated in Figure 3 but obtainable from it by taking at each energy the difference between unity and the sum of the other probabilities) increases. This is a superficially paradoxical result since one might expect that the opening up of additional channels which compete with the elastic one should decrease the probabilities for elastic collisions. The fact that this is not so is a direct manifestation of the quantum mechanical optical theorem, the paradox being due to an inappropriate application of classical mechanical ideas. The fact that reaction products with different vibrational quantum numbers from those of the reagent are formed is the manifestation of the breakdown of vibrationally adiabaticity as the collision energy increases. The fact that as more channels open up the value for transition probabilities into each channel (averaged over the oscillations) decreases is the manifestation of a very approximate statistical type behavior.

Figure 5 indicates the translational energy dependence of the reaction probability for reagent molecules in the first electronically excited state. Comparison with Figure 1 indicates that at about .85 eV total energy (corresponding to about .58 eV translational energy for ground state reagent) the total reaction probability for ground state reagent is about 80%, whereas that for first excited state reagent is about 6% only. Therefore, for total energies slightly in excess of those needed for the first vibrationally excited state of the reagent to be accessible the reaction probability for the ground state reagent is far in excess of that for its first excited state. This seems to be

a dynamic characteristic of the H_3 surface which need not be and probably is not valid for surfaces of different shapes. A much more detailed presentation of these and similar curves and of their physical interpretation as well as a comparison with classical calculations on the same surface will be published elsewhere. It should be noted that definite quantum effects are clearly present in this system.

7. A NEW NUMERICAL TECHNIQUE

The boundary value method used in the present calculations has the inconvenience of requiring the inversion of large banded square matrices of dimensions of several thousand and of band widths of several hundred. As a result large amounts of fast computer memory are necessary. We have been developing a new numerical technique aimed at overcoming this difficulty and at speeding up the calculations by one or more orders of magnitude. One of these methods consists in performing such banded matrix inversions by a technique in which a major fraction of the calculation is independent of the total energy of the system. Since the study of chemical reactions involves calculations at several tens of values of the energy, this may afford a substantial decrease in the computational time.

In another method we expand the 2-MD wavefunction in different sets of basis functions for different regions of the domain of the independent variables. In the reagent region these are the eigenfunctions of the reagent molecule, in the interaction region they are the eigenfunctions

of the transverse mode of the transition state, and in the product region they are the eigenfunctions of the product molecule. In addition, the independent variables used in each of these three regions are different. In the reagent region they are the reagent molecule internuclear distance, x_2 , and a scaled distance, x_3 , of the reagent atom to the center of mass of the reagent molecule. In the product region they are the internuclear distance of the product molecule, z_2 , and a scaled distance, z_3 , of the product atom to the center of mass of the product molecule. In the interaction region they are the circular polar coordinates, R and φ , with respect to an origin located sufficiently inside the high plateau region of the potential energy function for the wavefunction to be effectively zero at that point. Starting from the reagent region the matrix Schrödinger equation in the independent variable, x_3 , is integrated numerically up to the interaction region. The solution is then joined smoothly to the one in that region. The new matrix Schrödinger equation in the independent variable, φ , is then integrated numerically up to the product region. Once more the solution is joined smoothly to the one in that region. Finally, the matrix Schrödinger equation in the independent variable, z_3 , is integrated numerically out into the region of zero interaction. With this device essentially all of the numerical and analytical techniques developed for nonreactive scattering become applicable to reactive scattering. The speed-up comes from having transformed the two-mathematical dimensional problem into a one-dimensional one.

The computational effort associated with the other dimension is again independent of the total energy of the system and need be done only once for each reaction. This method is also being applied to the solution of the problem of reactive collisions on a plane.

8. PROGNOSIS FOR EXACT QUANTUM MECHANICAL CALCULATIONS

With the presently available generation of computers it is likely that the following "exact" quantum mechanical reactive scattering calculations will be performed within the next couple of years.

1. Linear Triatomic Systems

- (a) An extensive study of the dynamics of different families of electronically adiabatic triatomic surfaces including an analysis of the effect and disposal of vibrational and translational energy.
- (b) Electronically nonadiabatic triatomic reaction involving two interacting potential energy surfaces.
- (c) Collinear tetraatomic reactions on single electronically adiabatic surfaces.

2. Planar Systems

- (a) A moderate number of electronically adiabatic triatomic reactions with investigation of the effect and disposal of angular momentum.
- (b) A small number of electronically adiabatic tetraatomic reactions.

3. Three Physical Dimension Systems

- (a) A very small number of electronically adiabatic triatomic reactions.

The basic goal which motivates the implementation of such exact quantum mechanical calculations on realistic model potential energy surfaces is the production of computer-experimental data of good accuracy to be used for the development and testing of good approximate models of the dynamics of simple reactions. These models can then, hopefully, be applied with adequate reliability to other reactions involving a larger number of degrees of freedom. In addition, it would be desirable to establish reliable correlations between the shapes of multidimensional potential energy surfaces and their dynamical properties, usable for a wide variety of reactions.

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FIGURE CAPTIONS

- Fig. 1 Probability of reaction as a function of relative translational energy. Reagent molecule is in its ground vibrational state.
- 2-MD -- two mathematical dimensional calculation
VA -- vibrationally adiabatic model
CVE -- conservation of vibrational energy model
- Fig. 2 Potential energy barriers as a function of reaction coordinate.
- Fig. 3 Transition probabilities as a function of total system energy. P_{ij}^R and P_{ij}^V are respectively the reactive and nonreactive transition probabilities for the $(i - 1)$ th vibrational state to the $(j - 1)$ th vibrational state of the diatomic molecule. The T indicates the energy of the first vibrationally excited state of the reagent molecule.
- Fig. 4 Transition probabilities as a function of relative translational energy for ground vibrational state reagent. The T indicates the energy at which the second vibrationally excited channel opens.
- Fig. 5 Reaction probabilities as a function of relative translational energy. Reagent molecule is in its first vibrationally excited state.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5