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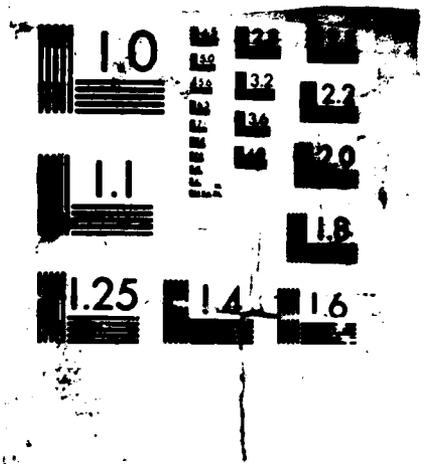
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in which $\langle E^* \rangle$ is the average energy of the transition state, $\langle E_0 \rangle$ is the

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Monte Carlo Simulation of Primitive Atom-transfer
Reactions in Solution

by

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Oakland University
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Monte Carlo Simulation of Primitive Atom-transfer Reactions
in Solution

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Abstract

The objective of this work is to develop a computational algorithm which combines saddle point and Metropolis/Monte Carlo optimization to investigate reactions in solution; the reactions involve atom transfer on an adiabatic potential energy surface. We seek a method to calculate the value of the rate constant in the form of the simple Arrhenius equation for the jump rate ν ,

$$\nu = \langle \omega \rangle \exp[-(\langle E^\ddagger \rangle - \langle E^0 \rangle)/kT],$$

in which $\langle E^\ddagger \rangle$ is the average energy of the transition state, $\langle E^0 \rangle$ is the average energy of the initial state, and $\langle \omega \rangle$ is the average frequency of passage through the transition state. Individual configurations in the Metropolis sample allow either for passage of the reactive species over the top of the barrier or tunnelling through the barrier. The average frequency $\langle \omega \rangle$ reflects this situation. Because the Metropolis sampling method deals with discrete collections of particles, with specified forces of interaction, the transfer frequencies for over-the-top of the barrier and tunnel transfers can be determined in terms of the actual interactions used instead of using non-specific, model potential energy functions for the barrier.

Introduction

Numerical saddle point methods are available to determine the location of the transition state for chemical reactions which involve atom transfer;¹ these methods generally have been used to determine the configuration of the transition state as a single configuration on an adiabatic potential energy surface for a reaction in vacuum. Although these calculations are routinely carried out, they have not been generally applied to reactions which take place in solution. Our purpose is to develop an algorithm which combines saddle point optimization with Metropolis/Monte Carlo sampling^{2,3} in order to determine values of rate constants for reactions in solution. No new theory is developed here; we work within the structure of the transition state theory. We assume that the relatively simple Arrhenius form of the rate constant,

$$k = A \exp(-E_a/kT), \quad (1)$$

applies and that it is possible to estimate the activation energy E_a as the difference of the average energies of the transition state, $\langle E^\ddagger \rangle$, and the initial state $\langle E_0 \rangle$. The pre-exponential frequency factor is predominantly an average of the frequency of passage through the transition state.

An important aspect of this work, we believe, is the fact that it is possible to calculate the activation energy and the pre-exponential frequency factor in terms of the discrete configurations of particles generated in the Metropolis sample together with the actual forces which one chooses to represent the interparticle interactions. It is not necessary, for example, to use non-specific (and often one-dimensional) models of the barrier in the transition state. As a result, it is possible to carry out

calculations which are more sensitive to the structure and nature of the interactions in the reactive system plus solvent.

In the following sections, we discuss the evolution of a reaction with the use of the Monte Carlo simulation. An important issue is the weighting of the distribution in a way which samples the transition state. Given adequate sampling, it is possible to examine each configuration to determine the how the reactive system passes through the transition state: either by passing over the barrier or by tunnelling through it. The methods are illustrated with a simple example, namely, the inversion of a bent molecule of the form ABA in a two-dimensional solvent of Lennard-Jones disks.

Metropolis Sampling and the Transition State

Metropolis sampling is an energy minimization technique.³ This is an important consideration when one attempts to sample configurations of the transition state ensemble. The Metropolis sampling algorithm is well known and documented. Averages of various quantities of interest can be computed directly as the ensemble of systems evolves:

$$\langle q \rangle = \frac{1}{N} \sum_{i=1}^N q_i \quad (2)$$

for N samples where q_i is the value of the variable q in the i^{th} configuration of the Metropolis sample.

There are two ways to apply Metropolis sampling to the investigation of the transition state. In the first method, a saddle point optimization to the transition state is calculated from the initial state configuration. This is clearly the most rigorously correct approach. However, it is the most costly path; saddle point optimizations are not generally fast or efficient. On the other hand, for the second method, the distribution can be biased so that configurations of the transition state are sampled in the

same manner as one samples configurations of the initial state. This approach is computationally much more efficient. The latter approach is the one we take.

We consider reactions which can be followed by following the migration of a definite atomic or molecular species. The inversion of a bent molecule ABA in a two-dimensional solvent is one example:



Another example is the transfer of an atom in a bimolecular reaction of the type



In each case, the location of a particular atom with respect to the others allows one to follow the reaction; the atom B in the ABA inversion and the atom Y in the XY + Z to X + YZ transfer will be referred to as "transfer species" in the remainder of the paper.

Given any individual configuration of the transition state as generated in an appropriate Metropolis cycle, the transfer species can execute only one of two types of motion in the transition state:⁴ *locally stable* or *locally unstable* motion. The stability of the motion is measured along to the transfer axis and is determined with respect to the interaction of the transfer species with all the remaining particles in the instantaneously rigid surroundings of the configuration.

In the first case, the transfer species occupies a local energy well in the instantaneous configuration of all the other atoms in the transition state. We assume that a configuration in which the transfer species is carried to and on through the transition state in a local energy well contributes to the totally adiabatic limit of the reaction; the transfer is both electronically and, with respect to the solvent, vibrationally

adiabatic. On the other hand, if the transfer species is locally unstable in the transition state, it must actually reach some state near to the transition state and tunnel through the remainder of the barrier.

In view of the fact that there is only one of two possible modes of transfer through the transition state for each configuration, the jump rate ν can be expressed as the simple Arrhenius formula

$$\nu = \langle \omega \rangle \exp[-\beta(\langle E^\ddagger \rangle - \langle E_0 \rangle)] \quad (3)$$

in which the energy difference is the activation energy and $\langle \omega \rangle$ is the average value of the frequency factor for the transfer, $\beta = 1/kT$:

$$\langle \omega \rangle = \frac{1}{N} \sum_{i=1}^N \omega_i \quad (4)$$

and

$$\omega_i = \begin{cases} \omega_a & \text{for an "over the barrier" transfer} \\ \omega_d & \text{for a tunnel transfer.} \end{cases} \quad (5)$$

In the next section, we outline the test for *local* mechanical stability of the transfer species. Following that discussion, we illustrate the technique by applying it to the case of the inversion of SO_2 for which there is a good analytical potential energy function. In the remaining sections of the paper we consider the calculation of the transfer frequency for passage over the barrier and for tunnelling through the residual barrier.

Analysis of Mechanical Stability

The transition state is characterized by *global* mechanical instability. Nevertheless, it is possible for the migratory atomic or molecular species to occupy a state in the transition state which is *locally* mechanically stable.⁴ It is necessary to be able to test any given configuration of the ensemble of transition states to see if this condition is satisfied.

It is possible to consider the stability of the motions of the transfer species within a given field of the surrounding atoms of the reactants in their configuration in the transition state. The determination is made using the second order coefficient of the Taylor series of the potential energy function of the system expressed in terms of symmetry adaptable functions, namely, the spherical harmonic functions.⁵

The interactions between atoms within a molecule can be expressed adequately in terms of a collection of two-center, three-center and higher order functions. The two-center contributions to the potential energy function can assume familiar forms such as the Morse, Lennard-Jones or Rydberg functions. The three-center and higher order terms can be expressed as polynomial functions in terms of the bond variables, $\rho_i = R_i - R_i^0$ and a range function that ensures the appropriate limiting behavior on dissociation (cf. Murrell, ref. 6).

A general potential energy function can have an angle-dependence:⁵

$$F(\mathbf{r}) = f(r)Y_{\lambda\mu}(\hat{\mathbf{r}}) \quad (6)$$

in which the angular part is contained in the spherical harmonic function $Y_{\lambda\mu}(\hat{\mathbf{r}})$ and $f(r)$ is the radial part. Complicated angular dependencies clearly can be constructed as sums of products of spherical harmonic and radial components. A scalar function has the simple representation

$$V(\mathbf{r}) = \sqrt{4\pi}Y_{00}(\hat{\mathbf{r}})v(r). \quad (7)$$

The expansion of this particular (scalar) function as a Taylor series has the form

$$V(\mathbf{R} + \mathbf{r}_1 - \mathbf{r}_2) = (4\pi)^{3/2} \sum_{n=0}^{\infty} \sum_{s=0}^n \binom{n}{s} r_1^{n-s} (-r_2)^s A_{n-s, \ell_1} A_{s, \ell_2} \sum_{(l, m)} [(2\ell_1 + 1)(2\ell_2 + 1)(2\ell + 1)]^{-1/2} (\ell_1 \ell_2 m_1 m_2 | \ell m) (\ell_1 \ell_2 00 | \ell 0) Y_{\ell_1 m_1}(\mathbf{r}_1) Y_{\ell_2 m_2}(\mathbf{r}_2) Y_{\ell m}(\mathbf{R}) I_{n\ell}(\mathbf{R}) \quad (8)$$

for which $A_{n\ell}$ is given by

$$A_{n\ell} = \frac{n!(2\ell + 1)}{(n - \ell)!!(n + \ell - 1)!!} \quad \text{for } n \geq \ell \text{ and } n - \ell = \text{even}$$

$$= 0 \quad \text{for } n < \ell \text{ and } n - \ell = \text{odd} \quad (9)$$

and $I_{n\ell}(\mathbf{R})$ is given by

$$I_{n\ell}(\mathbf{R}) = (-1)^{n+\ell} R^\ell \left[\frac{d}{R dR} \right]_{\mathbf{R}}^{\ell} \frac{1}{R} \left[\frac{d}{dR} \right]_{\mathbf{R}}^{n-\ell} v(\mathbf{R}) \quad (10)$$

$(\ell_1 \ell_2 m_1 m_2 | \ell m)$ is the Clebsch-Gordan coefficient and $\binom{n}{s}$ is the binomial coefficient.

At any given point of expansion, it is possible to transform to a Cartesian representation. For the first and second order terms, in particular, one finds

$$V^{(1)} = (\mathbf{r}_1 - \mathbf{r}_2) \cdot \hat{\mathbf{R}} I_{11}(\mathbf{R}) \quad (11)$$

where $\hat{\mathbf{R}}$ is the unit vector, and

$$V^{(2)} = (\mathbf{r}_1 - \mathbf{r}_2)^T \mathbf{K} (\mathbf{r}_1 - \mathbf{r}_2). \quad (12)$$

In a Cartesian representation, the elements of the force constant matrix \mathbf{K} are

$$k_{11}^{IJ} = \frac{1}{3} \left[I_{20}(\mathbf{R}) + (X_i^2 - X_j^2 - X_k^2) I_{22}(\mathbf{R}) / R^2 \right] \quad (13)$$

for the Cartesian diagonal terms and

$$k_{ij}^{IJ} = X_i X_j I_{22}(R)/R^2 \quad (14)$$

for the Cartesian non-diagonal contributions. In these expressions, R is

$$R = R_I - R_J,$$

the distance between the points I and J . The lower case indices cover the three Cartesian coordinates x , y , and z .

If $I = 0$ is the label of the transfer species within the field of the atoms in the transition state, then stability of that species is determined by the examination of the eigenvalues of the 3×3 matrix of local force constants. The elements of the stability matrix are found with

$$k_{ij} = \sum_{J=0}^N k_{ij}^{0J}(R_{0J}). \quad (15)$$

Let the eigenvalues of the k -matrix be κ_i where $i=1,2,3$. Stable motion of the transfer species in the transition state is guaranteed only if

$$\kappa_i > 0, \quad \text{all } i \quad (16)$$

In this case, then, the transfer species occupies an energy well in the transition state configuration. The entire transition state, however, is still globally unstable.

On the other hand, if $\kappa_i < 0$ for any single i ($=1,2,3$), the transfer species cannot occupy an energy well in the transition state. It is necessary for the particle to tunnel through the remaining barrier to the final state. This problem is considered shortly.

Example: Stability of the Linear Transition State of Sulfur Dioxide

In order to illustrate the test for mechanical stability, we apply it to a simple inversion in sulfur dioxide for which a good potential energy function exists, namely the Murrell *et al.* potential.^{6,7}

Consider the configurations illustrate in Figure 1. The initial state

of SO_2 is bent. In vacuum, the transition state for the inversion is linear. By symmetry, the motion of sulfur along the O-O line will be stable. The motion of sulfur along the transfer axis perpendicular to the O-O line may or may not be stable. As a result of the symmetry of the system, the axial force constant can be expressed as^{5a}

$$k_2 = -\frac{1}{3} \sum_I [I_{20}(R_I) - 2P_2(\cos \theta_{RI})I_{22}(R_I)] \quad (17)$$

where $P_2(\cos \theta)$ is the second order Legendre polynomial and θ_{RI} is the angle between the vector R_{I0} and the transfer (z) axis. The quantities I_{20} and I_{22} are simply⁸

$$I_{20}(R) = \frac{d^2V}{dR^2} + \frac{2}{R} \frac{dV}{dR} \quad (18)$$

and

$$I_{22}(R) = \frac{d^2V}{dR^2} - \frac{1}{R} \frac{dV}{dR} \quad (19)$$

The Murrell potential is the sum of contributions. The first terms are pairwise Rydberg terms

$$V_p(R) = -D \left[1 + \sum_{i=1} a_i \rho^i \right] \exp(-a_i \rho), \quad (20)$$

where D is the dissociation energy, $\rho = R - R_0$ and the a_i are coefficients in the functional form of the potential. The remaining contributions come from many-body terms:

$$V_{mb}(R) = V_0 \prod_{i=1}^N [1 - \tanh(\gamma_i S_i / 2)] \left[1 + \sum_i c_i \rho_i + \sum_{i < j} c_{ij} \rho_i \rho_j + \dots \right] \quad (21)$$

R is the set of atomic coordinates. The quantity S_i is

$$S_i = \sum_j b_{ij} \rho_j \quad (22)$$

and the transformation matrix b is determined by symmetry. The remaining quantities, γ_i and c_i , c_{ij} , etc. are determined by fitting the potential to various data--spectroscopic and *ab initio* calculations.^{6,7}

The values of the various coefficients were taken from Carter *et al.*⁷

The R_{∞} distance is simply twice the R_{50} distance in the transition state. The energy of the system in its linear transition state is plotted in Figure 2 as a function of the R_{50} distance. The equilibrium SO bond length is 1.431 Å. There are two energy minima along the OSO linear expansion in the transition state: the first is approximately 1.35 Å. Figure 3 shows the stability of the motion of the sulfur atom with reference to a displacement along the transfer axis in the transition state. It is clear from the figure that at the lowest energy of the system in the transition state, approximately 1.35 Å, the sulfur atom cannot occupy a position of stable mechanical equilibrium. This is true for both the pair potential and the many-body contribution. As a result, one anticipates that any inversion of the SO_2 molecule would involve the tunnelling of sulfur through the O-O line.

An interesting feature of Figure 3 is the relatively small range of values of R_{50} which admit over-the-barrier transfers of the sulfur atom. The stability of the Rydberg part of the whole potential energy function is standard for pair-potentials; the behavior of the Rydberg potential is similar to that of the Morse or Lennard-Jones potentials. The many-body part of the whole potential function does not admit any stable configuration for sulfur in the linear transition state. This can be seen to be the result of a strong restoring force for the bending mode. The combination of pair- and many-body (angle bend) forces, however, does allow a small set of configurations for which it is possible for sulfur dioxide to invert by carrying the sulfur atom through the transition region in a potential energy well. Such a state involves the excitation of the SO stretch displacements to a considerable extent. As can be seen in the Figures, there is a second minimum configuration of the transition state at about 1.85 Å. It is unlikely that at ambient temperatures, for example, there would be any

significant population of states characterized by the lengthened O-S bonds. Therefore, on the basis of this examination, we are inclined to believe that sulfur would have to tunnel through the O-O barrier in most cases.

Similar stability conditions can be seen to arise out of more approximate representations of the angle bending motions. Smith and Overend,^{9a} for example, examined several potential energy functions as representations of the bending potential in bent triatomic molecules. Given the fact that the potential for the inversion of SO₂ must be a symmetric double well function, Smith and Overend examined the following form which is suggested by the Swalen-Ibers treatment of ammonia:^{9b}

$$V(\theta-\pi) = k(\theta-\pi)^2 + b \exp[-c(\theta-\pi)^2] \quad (23)$$

and the angle θ is measured from the linear transition state for the inversion. The coefficients k and b depend on the SO bond lengths:

$$\begin{aligned} k &= K \exp[A(R_1+R_2)] \\ b &= B \exp[\beta(R_1+R_2)] \end{aligned} \quad (24)$$

and $A < 0$, etc. Using eqs (23) and (24) in the equations to determine the stability in the linear triatomic, one finds

$$k = \frac{2\beta B}{R_{SO}} \exp(2\beta R_{SO}) \quad (25)$$

[note, in the transition state, $\theta = \pi$]. As $\beta < 0$, it is clear that $k < 0$ in accord with the results found above for the Murrell potential⁶ (β in this expression is not $1/kT$). As a consequence, accurately determined experimental force constants for the bending motions in a molecule can aid in the determination of the stability of the transition state of a reaction.

Frequency Factor for Completely Adiabatic Transfers

We consider the case for which the transfer species occupies a stable energy well in a single transition state configuration of the Metropolis

sample. The problem is to determine the frequency factor which is associated with the migrating particle in this case.

The test for stability of the migratory transfer species requires the determination of the eigenvalues of the force constant matrix for the motion of the transfer species in the fixed field of the surrounding atoms of solute and solute. If all of the eigenvalues are positive definite, all motions of the transfer species are locally mechanically stable. The oscillatory motion of the transfer species along the axis in the direction of the final state determines the frequency which is associated with the wholly adiabatic transfer. Let the z-axis be aligned with the tangent to the transfer-axis in the transition state. The force constant for harmonic motion of the migrating atom along this axis is

$$K = \frac{1}{3} \sum_I (I_{20}(R) + 2P_2(\cos \theta_{RI}) I_{22}(R_I)) \quad (26)$$

in which the summation is taken over all atoms in the surroundings. The frequency for the transfer is simply

$$\omega_s = 2\sqrt{K/m}, \quad (27)$$

where the factor of 2 arises via the same argument as used in the method of beats,¹⁰ and m is the mass of the transfer species. This frequency is used for a particular configuration in eq (5).

Frequency Factor for Tunnel Transfers

The accuracy of the frequency factor for a nuclear tunnel transfer depends on the accuracy with which one can describe the system in the first place. Extensive use has been made of one dimensional model potential energy functions as representations of the barrier. We have been able to show¹¹ recently that it is possible to get good agreement with experiment for the inversion tunnelling in the ammonia by using a representation which employs discrete pair-potentials for the NH interactions. Thus, in principle, if good model potential energy functions are known for the atomic pair interactions and the angle bending modes, it is possible to carry out accurate calculations to estimate the tunnel frequency.

We propose the following computational algorithm. Given a case for which tunnelling is required, locate the nearest positions of local stability in the regions of the initial and final states for the transfer species in the frozen configuration of the environment. [It is necessary to note that the initial and final states for the tunnel transfer are almost never the same as the thermodynamic initial and final states of the reaction.] The rationalization we use is that a fluctuation of the system will bring the transfer species close to the transition state. These positions of local mechanical stability can be found, for example, with the use of steepest descents routines.

Having determined stationary initial and final states for the calculation, it is necessary to carry out some form of separation of the local modes from those of the remainder of the system. It is also necessary to identify the perturbations which account for the tunnel transfer.

We assume that Born-Oppenheimer electronic states have been separated from molecular vibrations; the reactive subsystem migrates over an adiabatic

potential energy surface. We identify and separate local vibrational modes⁴ of the reactive solute from the remaining solvent with a second use of the Born-Oppenheimer-Holstein¹² adiabatic separation applied to the intra- and intermolecular vibrations. The procedure we follow for atomic motions is analogous to the method which is used for the electron transfer problem.^{13,14} The method works for the atom transfer for the reason that atom-tunnelling only occurs if the vibrational overlap factors are nonvanishingly small and interaction with solvent is relatively weak. This is so, of course, only for reasonably small separations between the initial and final states for the migration.

The reactive subsystem can be defined to consist of the underlying reactive solute and nearest neighbor solvent when that solvent interacts strongly with the solute. The point we make here is that molecular vibrations can be handled (certainly in the harmonic limit) reasonably accurately, if the number of atoms and molecules is not too large. Thus, it is possible, in principle, to define the reactive subsystem to consist of solute and sufficient solvent such that were any additional solvent considered, its effect would merely mimic the bulk properties of the solvent.

A general development of the Born-Oppenheimer-Holstein separation of local vibrational modes for a reactive system has been presented elsewhere;^{4a} we summarize that development. A plane is located at the saddle point for the reaction. Stationary initial and final states are located on either side of this plane. Functions associated with these states are basis functions for the description of the tunnel transfer. It is possible, as is shown in the Appendix, to include basis functions of the transition state itself in order to account for tunnel transfers which are oblique; that is, transfers which do not occur on a straight line from the

initial to the final state through the transition state.

The Hamiltonian operator for the complete system of reactant and surroundings is written simply as

$$H = H_r + H_{en} + V_r^{en} \quad (28)$$

in which H_r is the vibrational Hamiltonian operator for the reactant subsystem and H_{en} is the operator for the remainder of the system. The specific interactions between individual atoms of the reactive subsystem and atoms and molecules of the surrounding environment are contained in the term V_r^{en} ; these individual contributions can be enumerated.

As an example of the Born-Oppenheimer-Holstein separation, we consider the specific separation for the two-state system which applies when the the transfer takes place only between ground initial and final vibrational states. The specific formulae that result should be generally applicable because of the great probability of a tunnel transfer between the ground initial and final states which have been adiabatically formed. Locally, one finds

$$H_r X_{I(F)} = \epsilon_{I(F)} X_{I(F)} \quad (29)$$

In terms of a basis set which is orthonormal with respect to the initial and final states, the overlap matrix is

$$S = \begin{pmatrix} 1 & S_{IF} \\ S_{IF} & 1 \end{pmatrix} \quad (30)$$

The inverse is

$$S^{-1} = \frac{1}{1 - S_{IF}^2} \begin{pmatrix} 1 & -S_{IF} \\ -S_{IF} & 1 \end{pmatrix} \quad (31)$$

The state function is constructed as

$$\Psi = f_I X_I + f_F X_F. \quad (32)$$

The expansion coefficients $f_{I(F)}$ are functions of the set of environmental coordinates of the solvent and molecular framework of the reactive solute.

In the usual manner, write

$$H\psi = E\psi \quad (33)$$

and

$$\langle \chi_I | H | \psi \rangle = E \langle \chi_I | \psi \rangle \quad (34)$$

Upon expansion,

$$\begin{aligned} E(f_I + S_{0J} f_J) = & \langle \chi_I | H_r + V^{en} | \chi_I \rangle f_I + \langle \chi_I | H_r + V^{en} | \chi_J \rangle f_J \\ & + \langle \chi_I | H_{en} | \chi_I \rangle f_I + \langle \chi_I | H_{en} | \chi_J \rangle f_J \end{aligned} \quad (35)$$

V^{en} contains all the interactions which depend upon coordinates of the reactive subsystem and the environment. Rewrite eq. (35) as

$$\sum_j S_{ij} (E - \epsilon_j - H_{en}) f_i = \sum_j (V_{ij} (1 - \delta_{ij}) + V_{ij}^{en}) f_j \quad (36)$$

This equation can be written more transparently as the matrix equation

$$SHF = VF \quad (37)$$

where H is the matrix

$$H = \begin{pmatrix} E-H_{en} - \epsilon_a & 0 \\ 0 & E-H_{en} - \epsilon_b \end{pmatrix} \quad (38)$$

In this equation, H_{en} is the Hamiltonian operator for the solvent species without the specific interaction between solute and solvent. F is the vector

$$F = \begin{pmatrix} f_a \\ f_b \end{pmatrix} \quad (39)$$

and V is the matrix

$$V = \begin{pmatrix} V_{aa}^{en} & V_{ab} + V_{ab}^{en} \\ V_{ba} + V_{ba}^{en} & V_{bb}^{en} \end{pmatrix} \quad (40)$$

In this expression, V_{ij} without the superscript index "en" indicates a matrix element which involves the interaction between the initial and final state configurations and the migratory species. These interactions are contained

within the operator H_r . We have ignored matrix elements which involve the momentum operators. They can easily be included in this general term. In analogy to the electron transfer case, the matrix elements V_{ij} account in large part for the perturbations which drive the tunnel transfer.

At this point, one can write

$$HF = S^{-1}VF \quad (41)$$

Upon expansion and rearrangement of this equation, we find the equation of motion for the coefficient f_a , for example,

$$\begin{aligned} \left[E - H_{aa} - \epsilon_a - \frac{1}{1 - S^2} (V_{aa}^{en} - S(V_{ba} + V_{ba}^{en})) \right] f_a \\ - \frac{1}{1 - S^2} (V_{ab} + V_{ab}^{en} - SV_{bb}^{en}) f_b \end{aligned} \quad (42)$$

With the use of this equation, the matrix element L_{IF} which accounts for the tunnel transfer can be identified:

$$L_{ab} = \frac{1}{1 - S^2} (V_{ab} + V_{ab}^{en} - SV_{bb}^{en}) \quad (43)$$

with a similar term for L_{ba} for the reverse transfer.

For an individual configuration of the ensemble, a transfer across the barrier takes place in the $0^\circ K$ limit. The tunnel frequency is calculated with the use of the "Golden Rule" expression:

$$w_{if} = \frac{2\pi}{\hbar} \sum_f |L_{if}|^2 \delta(E_i - E_f). \quad (44)$$

Assuming harmonic environmental modes and the Condon approximation for the matrix element L_{if} , it is possible to complete the summation over final states. The result is

$$w_{if} = \frac{2\pi}{\hbar} |L_{if}|^2 \exp(-\alpha^2 q_0^2 / 2) \frac{(\alpha^2 q_0^2 / 2)^n}{\hbar \omega n!} \quad (45)$$

where ω is the frequency of the accepting/donating mode and

$$\alpha = \sqrt{m\omega/\hbar} \quad (45)$$

and q_0 is the (dimensionless) equilibrium coordinate of the normal accepting/donating mode. The number n is fixed by energy conservation:

$$|E_0| = n\hbar\omega \quad (46)$$

and E_0 is the energy difference between the initial and final states.

The energy $\hbar\omega$ in the denominator of eq (45) comes from the approximation of the density of states of the manifold as $1/\hbar\omega$ (Siebrand, ref 15). This is an approximation which has proved to be inadequate for the radiationless transition in benzene. It is clear that some better approximations will have to be used to obtain accurate estimates of the tunnel frequency. For the moment, the expression (45) serves to identify the route which we suggest to follow in order to determine the transfer frequency. There is indeed another, even more approximate, route to follow: one can use the simple method of beats for which the transfer frequency is given by¹⁰

$$w_{if} = \frac{2|L_{if}|}{\hbar} \quad (47)$$

This expression will be reasonably accurate whenever the energy difference between the initial and final state energy wells is vanishingly small. This expression is the one which we use in the model simulation of the next section.

Example: Rate of Inversion of a Bent ABA Molecule

The reaction we simulate is the hypothetical inversion of a bent ABA molecule, see reaction (a). The mass of the B-species is taken arbitrarily to be 12 au, viz., carbon. The purpose of this choice is to try to determine whether an atom of the mass of carbon tunnels to any extent.

The following interactions are used between the atoms of the solute and between the solute and solvent. First, the Lennard-Jones interaction is

used to describe the bonds between A and B. The interaction between the two atoms A, however, is modelled as harmonic. The reason for doing so lies with the fact that a Lennard-Jones potential is too "soft" in the dissociative region to account for the effect of other atoms of solute and solvent which in a real system would present an effective repulsion to the expansion of the A-A distance. Thus, with the use of the harmonic interaction, as opposed to the Lennard-Jones which would be more appropriate to the species in the gas phase, it is possible to model the effect of an atom transfer within a rigidly bound polyatomic molecule with the use of a minimal system as we have done here. Note, we have not used angle bend or higher order interactions in this calculation, as correctly we should do. The reason for omitting them is primarily due to the fact that we have not yet worked out a good way to approximate the interaction in a form which can be incorporated into the tunnel calculation. We are currently seeking ways to approximate these important interactions.

The solvent is modelled as a collection of uniform spheres of radius 2.8 A. A Lennard-Jones potential is also used to describe the interaction between the individual atoms of the solute and the solvent. Finally, the interactions between the molecules of solvent are also modelled as Lennard-Jones. The parameters are summarized in Table I.

We used Lennard-Jones potentials throughout the calculation in the interest of computational speed. The form of the potential used was

$$V_{LJ} = \epsilon(a/r)^6 \left[(a/r)^6 - 2 \right] \quad (48)$$

in which a is the distance for which $V_{LJ} = -\epsilon$. More elaborate potential energy functions usually require calls to exponential, error and similar functions. This fact can greatly increase the amount of time needed to carry out a large number of calculations.

In carrying out the calculation, we fixed the central B atom in the ABA

molecule at the center of the unit cell in the Metropolis system. The A-atoms and the solvent were free to move. The entire system was two-dimensional; the solvent was modelled as a collection of Lennard-Jones disks. In order to eliminate edge effects, the minimum image technique was used. The unit cell was surrounded by eight image cells. Each particle within the primary cell interacted either with another species in the cell or its nearest image if the image was closer. Sampling was carried out on a canonical ensemble.

The calculations required the use of the Cray XMP/24 computer in order to obtain results in reasonable time. The Metropolis simulation proceeded in two steps. First, the unconstrained optimization of the system was carried out in order to determine the average energy of the initial state. No other averages were determined. These optimizations were carried out for a sequence of temperatures beginning with a cycle at 4 K to 300 K. The simulation of the transition state involved calculations for the same sequence of temperatures as used in the determination of the initial state. The algorithm to determine the energy and frequency factor for the transition state, however, was considerably more complicated than that used in the determination of the initial state.

The vacuum transition state for the ABA system is the optimized linear configuration A-B-A. With the B-species fixed to the center of the unit cell, and the A-species constrained to move along the A-B-A line, the system was allowed to evolve configurations of the transition state in the following manner. Motion of the A-species along the A-B-A line was allowed together with motion of the solvent to optimum configurations. We made the assumption that the solute in its transition state could adiabatically adjust to the solvent. Thus, the Metropolis steps generated configurations of solute and solvent which were near to, but not exactly, the transition

state. In order to generate the final configuration which represented the transition state, we carried out a Newton-Raphson saddle point optimization of the ABA solute in the frozen solvent. We reasoned that the solvent would equilibrate to a configuration close to the transition state. Therefore, the equilibration of the solute in the rigid solvent would not return the solute to a ground or initial state configuration. In carrying out this kind of optimization to the transition state, it is clear that geometrically non-linear transition states are possible.

For each new configuration of solvent generated in the Metropolis sample, a Newton-Raphson optimization was carried out for the B-species alone to determine the nearest stationary states on the reactant and product sides in the frozen configuration of the transition state. Note, these initial and final states are not the thermodynamic initial and final states. They are states below the transition state barrier in which the B-species occupies a local energy well.

We found that on occasion, the routine would find two energy minima on the same side of the A-A line. In this case, the configuration was discarded and the last configuration kept. The test of whether the initial and final states are separated by the A-A line is simple. The directed distance from the line¹⁸

$$Ax + By + C = 0 \tag{49}$$

to the point (x_1, y_1) is

$$d_1 = \frac{Ax_1 + By_1 + C}{\pm(A^2 + B^2)^{1/2}} \tag{50}$$

In the same manner, the distance to a second point (x_2, y_2) from the same line is d_2 . If, then

$$\delta = (Ax_1 + By_1 + C)(Ax_2 + By_2 + C) > 0 \tag{51}$$

both the initial and final state lie on the same side of the A-A line. This

test is easily generalized to three dimensions; the A-A line is simply replaced by the dividing plane which contains the saddle point or some other suitably defined point of reference.

The mechanical stability of the migratory B-species was determined for each Metropolis element of the ensemble of transition states. If the species B proved to be stable in the presence of its environment of the A-species and the solvent, that element of the transition state ensemble was adiabatically attained. We then determined the frequency associated with the motion of B along the transfer axis according to eqs (26) and (27). This frequency was identified as ω_a and used in eq (4). If the B-species was found to be locally unstable in the transition state, then a tunnel frequency was calculated. This frequency was determined by the following sequence of steps.

The determination of the tunnel-transfer frequency was found by using a one-dimensional analysis along the transfer-axis. Thus, we considered only the direct, straight-line transfer from the initial to the final state. The basis functions are the simple ground state one-dimensional harmonic oscillator functions:

$$u_0(\alpha, z) = (\pi/\alpha)^{1/4} \exp(-1/2 \alpha z^2) \quad (52)$$

and a similar function for the final state (identified in the exponent by the coefficient β).

Let z be the transfer-axis. The potential energy operator can be written as¹⁰

$$V(z) = \sum_{n=0}^{\infty} z^n C_n(R) \quad (53)$$

where

$$C_n(R) = \frac{1}{n!} \sum_{l=0}^n A_{nl} \sum_{i=1}^N P_l(\cos \theta_{R_i}) I_l(R_i) \quad (54)$$

In these expressions, R represents the set of distances from the transfer-species to the collection of N solvent molecules and remaining atoms of the solute. The angle between the z -axis and the location of the species i at a distance R_i from the coordinate origin is θ .

The state function

$$\psi(z) = f_a u_0(\alpha, z) + f_b u_0(\beta, z) \quad (55)$$

yields the usual matrix elements which are needed to evaluate the frequency factor. The overlap S is

$$S = \left[\frac{2\sqrt{\alpha\beta}}{\alpha+\beta} \right]^{1/2} \exp\left[-\frac{\alpha\beta R^2}{2(\alpha+\beta)} \right] \quad (56)$$

and R is the distance between the initial and final locations of the B-species. We specifically need to evaluate the matrix element V_{ab} . This is

$$\begin{aligned} V_{ab} &= \langle u_0(\alpha, z) | V(z) | u_0(\beta, z) \rangle \\ &= \sqrt{2} \left[\frac{\alpha\beta}{\alpha+\beta} \right]^{1/2} \exp(-Q^2) \sum_{n=0}^{\infty} C_n(R_{I0}) \sum_{m=0}^{\infty} \binom{n}{m} (-d)^{n-m} [1 - (-1)^m] \\ &\quad \times (m-1)!! (\alpha+\beta)^{-m/2} \end{aligned} \quad (57)$$

where

$$Q^2 = \frac{\alpha\beta}{2(\alpha+\beta)} R^2 \quad (58)$$

and

$$d = \frac{\alpha l_a - \beta l_b}{\alpha + \beta} \quad (59)$$

The quantities l_a and l_b are the distances to the initial and final locations at a and b as measured from the origin on the z -axis. Finally, the quantity $C_n(R_{I0})$ is evaluated with the set of distances and angles measured with respect to the origin of coordinates on the B-species on the z -axis.

We made the assumption that the environmental factors V_{ij}^{en} contribute only a small amount to the total value of the matrix element and may, therefore, be ignored. This assumption can always be tested by direct computation whenever one suspects it is not reasonable. However, the combination of small overlap and large distances in $C_n(R)$ would seem to justify the neglect of these terms under most circumstances.

The frequency of the tunnel jump was evaluated with eq (47). The quantities α and β were determined in terms of the harmonic frequencies which could be assigned to the transfer-species in its initial and final locations.

The system consists initially of a simple square lattice at 4 K. Several runs were made at 4 K to "temper" the system. Next, runs were made at 50, 100, 200 and 300 K. This routine was followed both for the determination of the initial state energy (unrestricted Monte Carlo) and for the transition state calculations (biased in favor of the linear transition state for ABA).

The results of the calculations are summarized in Table II. As can be seen, two values of the (harmonic) A-A interaction were used. the "hard" harmonic interaction (viz., 8×10^5 dyn cm⁻¹) yields degrees of overall adiabaticity of reaction which are much smaller than those found with the smaller value of the A-A interaction (8×10^4 dyn cm⁻¹). Because of the weak A-A interaction in the first case, it is clear that the activation energy for this system, when it is positive at higher temperatures, is very small. As one would expect, with the stronger A-A interaction, the activation energy is larger, reflecting the work needed to stretch the A-A distance in the transition state.

There is a temperature-dependence in the frequency factor, to a degree. At low temperatures, below 100 K, the frequency factor increases with

decreasing temperature. At 200 K and above it appears to be essentially constant.

The degree of overall (electronic and vibrational) adiabaticity of the reaction is easily determined in the sampling cycle by assigning a value of unity to any configuration which admits an over-the-barrier transfer and zero to the cases for which tunnelling through the residual barrier is required. As one expects, in the system in which there is a strong A-A association, there will be a greater amount of tunnelling through the residual barrier in the transition state. This is clear from the fact that even at 300 K, the fraction of over-the-barrier transfers is only about 0.01.

A curious feature of these calculations is the fact that especially for the "weaker" force constant and at very low temperatures, the linear ABA species seems to be stabilized by the solvent as indicated by the apparent negative activation energies. It may be the case that at the low temperatures in particular, a very large number of cycles needs to be used in order to reach an accurate value of the initial state energy. It was clear from our results, however, that at the higher temperatures, the system clearly stabilizes for the number of cycles used (from 156,000 to 312,000).

Whether or not the solvent stabilization of the linear configuration at low temperatures for the weaker interaction is real needs to be examined in more detail. We did not determine average configurations of the initial state. We did keep a record of the average cartesian coordinates of the ABA atoms in the transition state calculations. For the case of the weak A-A interaction, we found that the average A-A separation was approximately 2.8 Å which is a very small extension over the equilibrium value of 2.75 Å. However, with the stronger interaction between the A-atoms, even this slight extension is reflected in a significant increase in energy. For the

stronger interaction, the average A-A distance in the transition state is approximately 2.78 Å. For both the "weak" and the "strong" A-A harmonic interactions, the transition state remained, on average, linear in the presence of solvent.

Discussion

The objective of this work is to model the transition state by a combination of saddle point and Monte Carlo optimizations. Metropolis sampling generates individual elements of the ensemble of configurations of the transition state. Saddle point optimization can then be applied to each configuration in order to generate an ensemble of individual transition states.

The general analysis we have outlined highlights the important features of the treatment. Many issues need to be explored and developed further. An important issue, which we have mentioned, but not included in the example calculation, has to do with the role of many-body interactions. These arise predominately as angle-bend interactions in vibrational spectroscopy in the harmonic limit. Bend-bend and bend-stretch interactions are manifestations of higher order many-body forces. The example of SO_2 , given earlier, shows that these higher order contributions cannot be neglected if one is to get an accurate estimate of the pre-exponential factor for the reaction. It does seem possible, on the basis of the Smith-Overend work on anharmonic interactions,⁹ to estimate these interactions with the use of vibrational spectroscopy of the initial and final states. The systematic investigation of this approach needs to be examined further, and we plan to do so.

There has been other work to apply Monte Carlo methods to the study of

chemical reactions. Doll and Adams¹⁷ in a series of papers have investigated the use of Metropolis sampling together with an improved version of Slater's¹⁸ theory of reactivity. They have applied their analysis to the thermal desorption problem. At first glance, our approach is similar to the Adams-Doll work. On closer examination, however, there are significant differences. Doll^{17a} proposed examining the expression

$$L(q) = \frac{1}{2} \langle \delta(x - q) \dot{x} \rangle \quad (60)$$

which yields the average number of zeros for the function $x(t) - q$ in an interval of time $0 \leq t \leq \tau$. The quantity q , in Slater's theory,¹⁸ is a critical distance for reactivity, a critical bond length or height of the barrier. Adams and Doll^{17b-d} replace the delta-function by a Gaussian and directly evaluate the average by the Metropolis technique. The value of q is specified. The specification of q is a restriction which is not satisfactory for reactions taking place in solution. As noted in the early work on the transition state theory,^{19,20} the quantity q in essence is the location of the hyperplane which passes through the transition state in the reaction hypersurface. This identification alone, however, is not sufficient to derive the final form of the transition state rate constant. Optimization needs to be carried out on the hyperplane in order to reach the true saddle point which is the transition state. It is this prescription which we have followed here. As we have noted, it is possible to assume that a transition state which is evaluated for the system in vacuum (in the absence of solvent) can be used as a template on which to bias the distribution to the transition state for the reaction in solution. Subsequent relaxation of the system to the true transition state in solution is needed. As a consequence, we do not see how Doll's approach can be directly extended to apply to the systems we consider.

In our work, we have not directly considered librational motions or

full rotational contributions to the transition state. Wardlaw and Marcus²¹ and Viswanathan *et al.*²² have investigated these issues in particular for reactions which take place in the gas phase. Librational motion, particularly for solution phase, is important, and, indeed, has not been neglected entirely in our work. The assumption of Born-Oppenheimer separability of the solute vibrational modes from degrees of freedom of the solvent shows how specific account of the librations is included. The issue is the matter of time-scales. The Metropolis samples we made primarily involved the displacement of solvent. The solute was then adjusted to the solvent by a steepest descent calculation. The validity of this sequence of steps rests on the assumption of the adiabatic separation of the solute intramolecular vibrations from the solvent center-of-mass motions; we did not consider the intermolecular coupling of internal molecular vibrations, although it is possible to do so. We assumed, however, that the center-of-mass motions of the solute were similar (in scale) from those of the solvent. Therefore, displacement of the solvent according to the Metropolis method should evolve on the same time-scale as libration of the solute. Librational contributions are then automatically included--but not distinguishable from solvent contributions--in the averages.

Librations are included in the determination of the tunnel transition probability. This is apparent in the analysis which separates the intramolecular solute vibrations from the remaining degrees of freedom of the solvent and center-of-mass motion of the solute. This is implicit (and can be made explicit with a vibrational analysis in the harmonic limit) in eq (28). Eq (45), in fact must be summed over all the modes which contribute. For a system of limited extent, this is in principle possible. However, even for the size of system which we have considered here, the determination of the eigenfrequencies for the vibrations together with the

sequence of steps for the Metropolis sampling would be very costly in computer time. This is one of the reasons why we opted to use the simpler expression eq (47) in this work.

Tapia and co-workers²³ have recently examined an actual reactive system in solution: the protonation of 3 methyl-but-1-yne-3-ol in water. In this work, however, they did not optimize the transition state in solution as we have done. Instead, they examined the role of solvent in the system in its initial, transition and final states; the transition state was frozen at the vacuum configuration. They indeed found that there were important solvent effects. They were not able, however, to investigate how the presence of the solvent can alter the structure and dynamics of the solute in the transition state in solution over that determined in vacuum. There is growing evidence²⁴ that the interaction of solute with solvent and with metal surfaces in many cases alters the bonding in a substrate sufficiently to see in the vibrational spectrum. Although a study of type of Tapia *et al.*²³ can yield interesting information about solvation and large scale changes in solvation in going from the initial to the transition state, it is probably not possible to obtain accurate estimates of other quantities associated with the transition state. We think that our approach may point to way to filling that need.

The Metropolis sampling algorithm is not the only possible means of modelling chemical reactivity. Recently, Wilson and Hynes and their co-workers²⁵ reported an extensive examination of the SN_2 type of reaction using molecular dynamics. Their approach is complimentary to ours in the sense that they also seek to follow the course of the reaction by employing adequate potential energy functions for the interactions. Chemical reactions are manifestly time-dependent phenomena, and, as such, it seems immediately clear that molecular dynamics is the most natural model to

express this fact. On the other hand, the transition state theory of reactivity makes extensive use of ensemble averages which can be examined in an essentially time-independent frame of reference. In this sense, the Metropolis/Monte Carlo may prove useful. This is our view.

Pursuing the comparison further, Wilson *et al.* used their molecular dynamics algorithm to construct the potential energy surface for the reaction. At the same time, however, they also examined the frequency of first passage, reflection and subsequent passage. Thus, they were able to estimate the transfer frequency from two points of view: one direct and the other through an analysis of passage over and tunnelling through the average barrier. There are issues which seem better handled with the molecular dynamics approach, *viz.*, the issue of "dynamic friction" and the question of the role of momentum in the approach to and passage over the barrier. In our approach, through the Monte Carlo algorithm, we seek to account for some similar factors through the detailed analysis of the tunnel frequency. It remains to be settled just how close the two approaches will come to each other. In general, the Monte Carlo approach is computationally cheaper; it is expected, therefore, that one day it may be useful in approximate, but still reasonably accurate and predictive, calculations which may become generally available.

No matter how simple the system, the examination of reactivity consumes great amounts of computer time, even on the fastest machines. We need to look for more direct, and probably approximate, methods to handle the solvent. As an alternative to scanning for meaningful minima, Warshel proposed several schemes,²⁶ one of which is his "surface constrained soft sphere dipole" model for use with polar solvents. This model is flexible and accurate, when applied to the determination of solvation enthalpies. As Warshel notes, the enthalpy is the leading term--the entropy is a second

order effect.

It would seem that Warshel's approach might apply to the determination of transition states and reaction rates as we have proposed here. There is, however, a problem which needs to be resolved before Warshel's model of the solvent can be combined with our approach. Warshel's technique is to build shells of solvent about the reactive solute.²⁶ The innermost shell is the most sensitive to states and changes of states of the solute. The next layer of solvent is constrained to the configuration of bulk solution. The states of the solute and strongly bound solvent can then be determined by means of steepest descents optimization, and, for the transition state, saddle point optimizations. The difficulty with this approach is the fact that static optimization of this type only finds one most probable configuration. Such a configuration may correspond either to a configuration which is completely adiabatically attained or to one for which a tunnel transfer is required. The balance between tunnel transfers and over-the-top passes is not possible.

Some form of sampling of the neighborhood of the transition state is needed in order to determine an accurate average value of the pre-exponential frequency factor. Warshel has already noted that it is possible to use Metropolis/Monte Carlo methods to sample states in the neighborhood of the optimally determined state, as found, for example, with the use of a steepest descent routine. In this way, one may be able to determine accurate values of the frequency factor with a modest expense in computer time.

Conclusion

We have suggested that the reaction rate constant can be constructed as

an ensemble average of configurations of the transition state which are generated according to a modified Metropolis sampling scheme. For each element of the collection of configurations in the ensemble of transition state configurations, the transfer species either occupies a local energy well or must tunnel through a residual barrier. A frequency factor can be determined for each case. The average of the frequency factors associated with these two possibilities in principle yields an accurate value of the pre-exponential frequency factor in the Arrhenius expression for the rate constant. We believe that the algorithm which we suggest shows some potential in helping us to examine complicated chemical reactions in solution.

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Appendix

Basis and State Functions for Use in Tunnelling Calculations

In this appendix, we outline a general method for determining state functions which can be used in tunnelling calculations. In order to construct a usable Born-Oppenheimer separation of the local modes from those of the surroundings, it is necessary to develop first an analysis of the reactive subsystem. Given a set of atomic and molecular species which make up the reactive molecular system, and given a set of realistic interaction potential energy functions, the first objective is to develop an analysis of the motions of the isolated molecular system. In order to be able to follow the tunnelling of the transfer species, it is necessary to identify the parts of the reactive subsystems and then to connect the separate parts

in an analysis which focuses on the terms which account for the transfer.

With special reference to the transfer species, there are three principal locations for this species: the initial configuration, the location of the transfer-species in the transition state, and finally the location of the species in the final state configuration. If the trajectory for the transfer-species is a straight line, it is possible to consider the tunnel transition only with reference to the initial and final stationary configurations. If the reaction path is geometrically non-linear, or oblique, it is necessary to consider a piece-wise linear transfer; precedent for this of course is the construction of basis sets of atomic orbitals in the familiar LCAO versions of the molecular orbital theory. An illustration of an oblique path for tunnelling is shown in Figure 4 for a hypothetical diffusion of a species from one vacancy to another.

Although the initial and final states are mechanically stable, the third location, the transition state, is not. Nevertheless, this state can be included in a linear combination in order to connect the initial with the final state along a piece-wise linear path.

We imagine a dividing plane in the transition state. Left/initial and right/final states are defined with respect to this plane. We next consider a set of harmonic oscillator basis functions which are centered at the initial, transition, and final states. Let the set be $\{u_i(r_I)\}$ where the index i is a function label and the index I is a label for the point of expansion. These functions are locally orthonormal with respect to the point of expansion. The form of the particular functions $u_i(r)$ is not important at this stage, but they are typically the spherical harmonic oscillator or similar functions.

We construct orthonormal functions for the initial and final states on either side of the dividing plane. These functions will be the basis

functions for the construction of a set of state wavefunctions for the system. The elements in the expansion must contain functions which are centered at the initial (or final) state and the transition state; the method has already been discussed for the case of proton transfer.²⁷ Thus, it is possible to allow for the transitory occupation of the transition state region by the particle. Functions of an orthogonal set can be written as

$$\phi_{L(R)j} = N_{L(R)j}^{1/2} \sum_{i,I} d_{iI} u_i(r_I) \quad (A1)$$

where the coefficients of expansion d_{iI} are determined by the Gram-Schmidt method. The label L(R) in eq (A1) indicates a function for the left (right) hand side of the transfer hyperplane. The functions $\phi_{L(R)i}$ are now used to construct the state functions for the motion of the particle on the left (right) hand side of the transfer plane:

$$\psi_{L(R)}^\mu = \sum_{L(R)j} a_{L(R)j}^\mu \phi_{L(R)j} \quad (A2)$$

where the index μ is an energy level index.

Eigenvalues and eigenvectors for the initial and final transfer states are determined on the left and right hand sides of the transfer plane; this is done, as usual, by means of a variational calculation. For $H_{L(R)}$ the local Hamiltonian operator for the motion of the transfer species on the left (right) of the transfer plane, a set of eigenvalues $(\epsilon_{\mu L(R)})$ results which are associated with the migratory species.

As long as the basis set only contains functions that allow for motion of the transfer species between two stationary points, the initial and the transition state or the transition and the final state, these functions alone cannot account for the complete migration.

Next the optimally determined local states ψ_L^μ are used to construct state functions for the whole transfer system: initial, transition and final

states. Orthonormal L/R functions are constructed by Gram-Schmidt orthogonalization:²⁸

$$\chi_{L(R)} = \sum_{\mu} D_{\mu L(R)} \psi_{L(R)}^{\mu} \quad (A3)$$

with the coefficients $D_{\mu L(R)}$ determined by the orthonormalization. The coefficients C_I (I=L,R) in the expansion

$$\Psi = \sum C_I \chi_I \quad (A4)$$

are determined by a variational calculation.

The result of all of these steps is the expression of the matrix elements for the transfer in terms of local functions $u_i(r_i)$ centered about each of the three primary points for the transfer: initial, transition and final states.

As an example, consider the special case of a ground state transfer. As basis functions, we use the ground state spherical oscillator functions:

$$u_0(r) = (a/\pi)^{3/4} \exp[-\frac{1}{2} ar^2] \quad (A5)$$

The orthonormal expansion functions for the left and right hand sides are

$$\phi_{L1} = u_0(r_a) \quad (A6)$$

and

$$\phi_{L2} = \frac{1}{(1 - S_{at}^2)^{1/2}} [u_0(r_t) - S_{at} u_0(r_a)] \quad (A7)$$

where S_{at} is the overlap between site a (on the left) and t in the transition state; there are similar terms for ϕ_{R1} and ϕ_{R2} . These functions now can be combined to get the left and right hand side state functions:

$$\psi_L = a_{L1} \phi_{L1} + a_{L2} \phi_{L2} \quad (A8)$$

$$\psi_R = a_{R1} \phi_{R1} + a_{R2} \phi_{R2}$$

The lowest eigenvalue for this set of basis functions is $\epsilon_{L(R)}^0$. We now construct the left and right orthonormal basis functions:

$$\chi_L^0 = \psi_L^0 \quad (A9)$$

$$X_R^0 = \frac{1}{(1 - S_{LR}^2)^{1/2}} \left[\psi_R^0 - S_{LR} \psi_L^0 \right]$$

and the overlap is expressed in terms of the basis functions $u_i(r_i)$. The system energies are now simply

$$E = \frac{1}{2}(H_{LL} - H_{RR}) \pm \frac{1}{2}((H_{LL} - H_{RR})^2 + 4H_{LR})^{1/2} \quad (A10)$$

where the matrix elements have an obvious origin. These matrix elements also can be expressed in terms of integrals of the basis set $u_i(r_i)$.

We now have a representation in which the transfer species is described in an initial or final state (left or right state) which includes an account of the link to the transition state. The expansion of the matrix element H_{LR} in eq (A10), for example, indicates a connection from the initial to the final state through the transition state.

There has been some discussion of this type of approach from the point of view of the Bardeen transfer matrix formalism.²⁹ The approach we advocate here, however, is slightly different. We assume that there exists a set of well behaved and denumerable potential energy functions which operate between the species in the system. We also assume that the structure of the system is known or at least specified. The transfer formalism, initiated by Oppenheimer,³⁰ works well for barriers which are not fully described, i.e., barriers of arbitrary extent and height. The transfer system, as we see it, is as well characterized as is the atomic substructure in a molecular orbital calculation. We simply partition the wavefunctions in such a manner as to reveal the interactions and matrix elements.

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Table I

Potential energy functions and parameters

Bond	Potential	ϵ/k	Characteristic distance
A-B	Lennard-Jones	$\epsilon = 2.5$	$a = 1.41 \text{ \AA}$
A-A	Harmonic	$k = 8(80)$	$r_0 = 2.75$
A-S	Lennard-Jones	$\epsilon = 0.05$	$a = 2.8$
B-S	Lennard-Jones	$\epsilon = 0.05$	$a = 2.8$

The form of the Lennard-Jones potential used is

$$V_{LJ} = \epsilon(a/r)^6 [(a/r)^6 - 2]$$

and the pair dissociation energy ϵ is expressed as $\text{erg} \times 10^{12}$. The harmonic potential is

$$V_H(r) = \frac{1}{2} k (r - r_0)^2$$

and k is expressed as $\text{dyn cm}^{-1} \times 10^{-4}$.

Table II

a. Computed quantities for the ABA inversion with $k = 8 \times 10^4 \text{ dyn cm}^{-1}$.

Temperature (K)	$\langle E_0 \rangle$	$\langle E^\ddagger \rangle$	$\langle \omega \rangle$	adiabaticity
4	-9.429	-9.594	0.334	0.0308
50	-9.413	-9.437	0.368	0.2298
100	-9.157	-9.233	0.190	0.7218
200	-8.782	-8.774	0.232	0.5862
300	-8.588	-8.587	0.240	0.4652

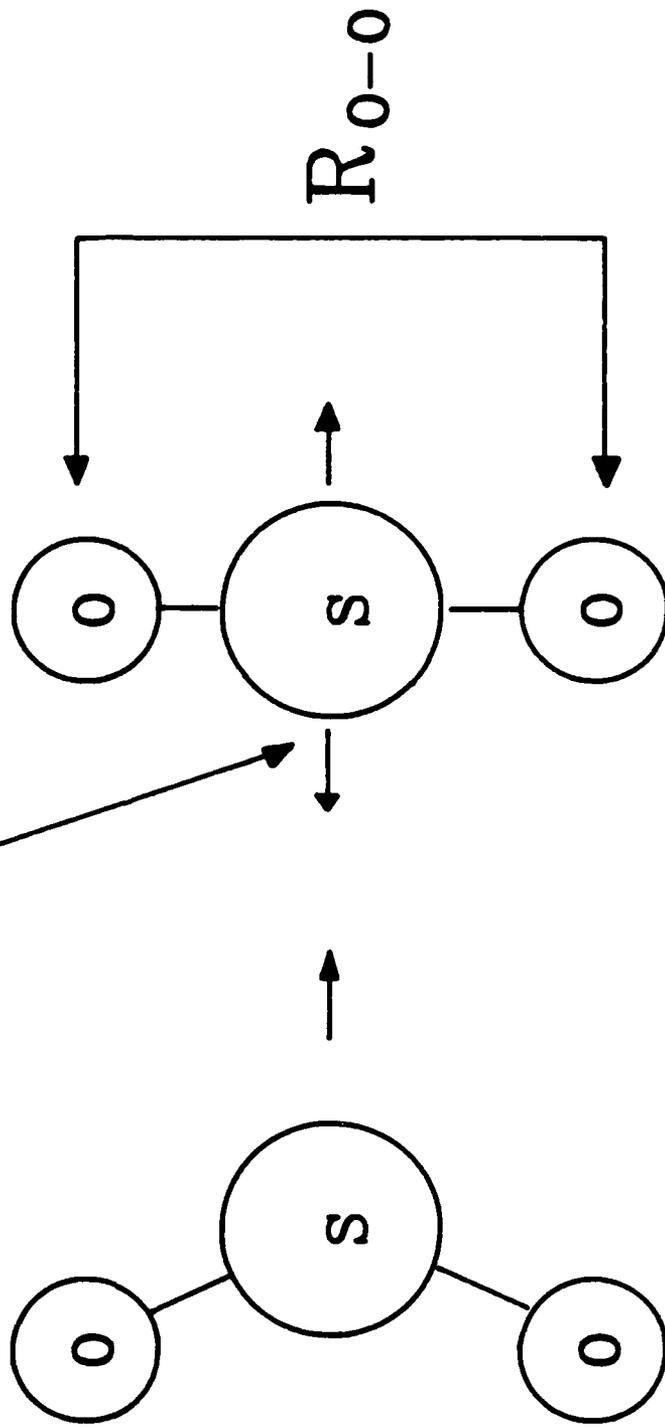
b. Computed quantities for the ABA inversion with $k = 8 \times 10^5 \text{ dyn cm}^{-1}$.

4	-9.484	-9.557	0.773	0.00001
50	-9.400	-9.311	0.405	0.0077
100	-9.262	-9.052	0.280	0.0145
200	-8.790	-8.686	0.263	0.0891
300	-8.568	-8.504	0.266	0.0884

Figure Captions

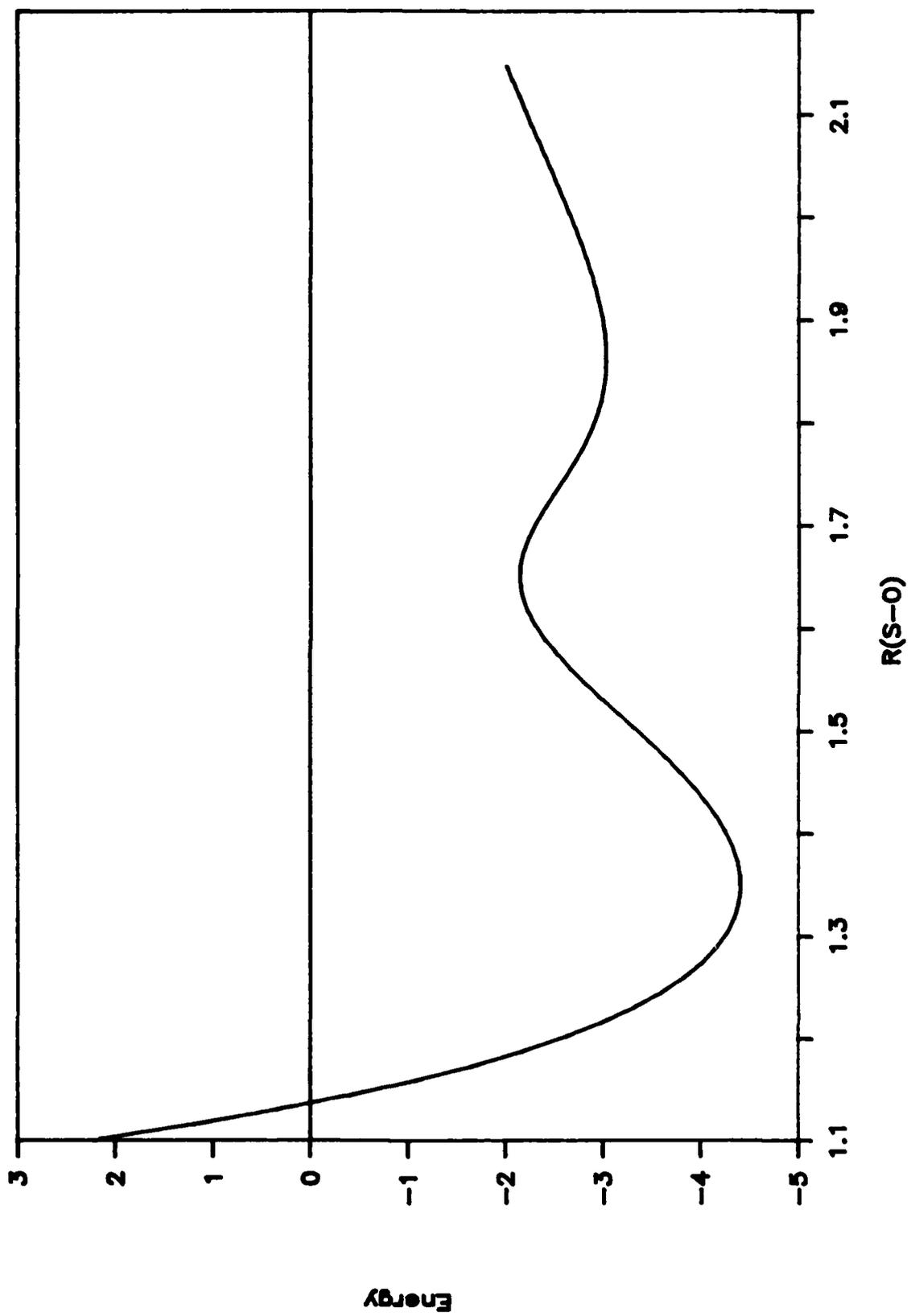
1. The initial and transition states for the inversion of SO_2 constrained to two dimensions.
2. The energy of linear SO_2 in the transition state for the inversion as a function of the SO bond distance. Only a symmetric stretch is considered. The energy is calculated with the use of the Carter, *et al.* potential (ref. 7).
3. The behavior of the second derivative of the potential energy [$E'' = d^2E/dz^2$] with respect to the displacement of the S-atom along the line normal to the O-O line. The curve labelled *a* is the behavior due to the Rydberg pair potential. The curve *b* is the behavior of the many-body part (which accounts for angle restoring forces). Curve *c* is the sum of *a* and *b*. The region of curve *c* above zero indicates the region of stability for the motion of S normal to the O-O line in the transition state.
4. The course of diffusion of an atom from one location to a vacancy along an oblique path. The transition state does not lie on the straight line from the initial to the final site. Account of the transition state can be incorporated in the analysis by mixing basis functions for the diffusing species at the location *t-s* with basis functions for the initial and final locations.

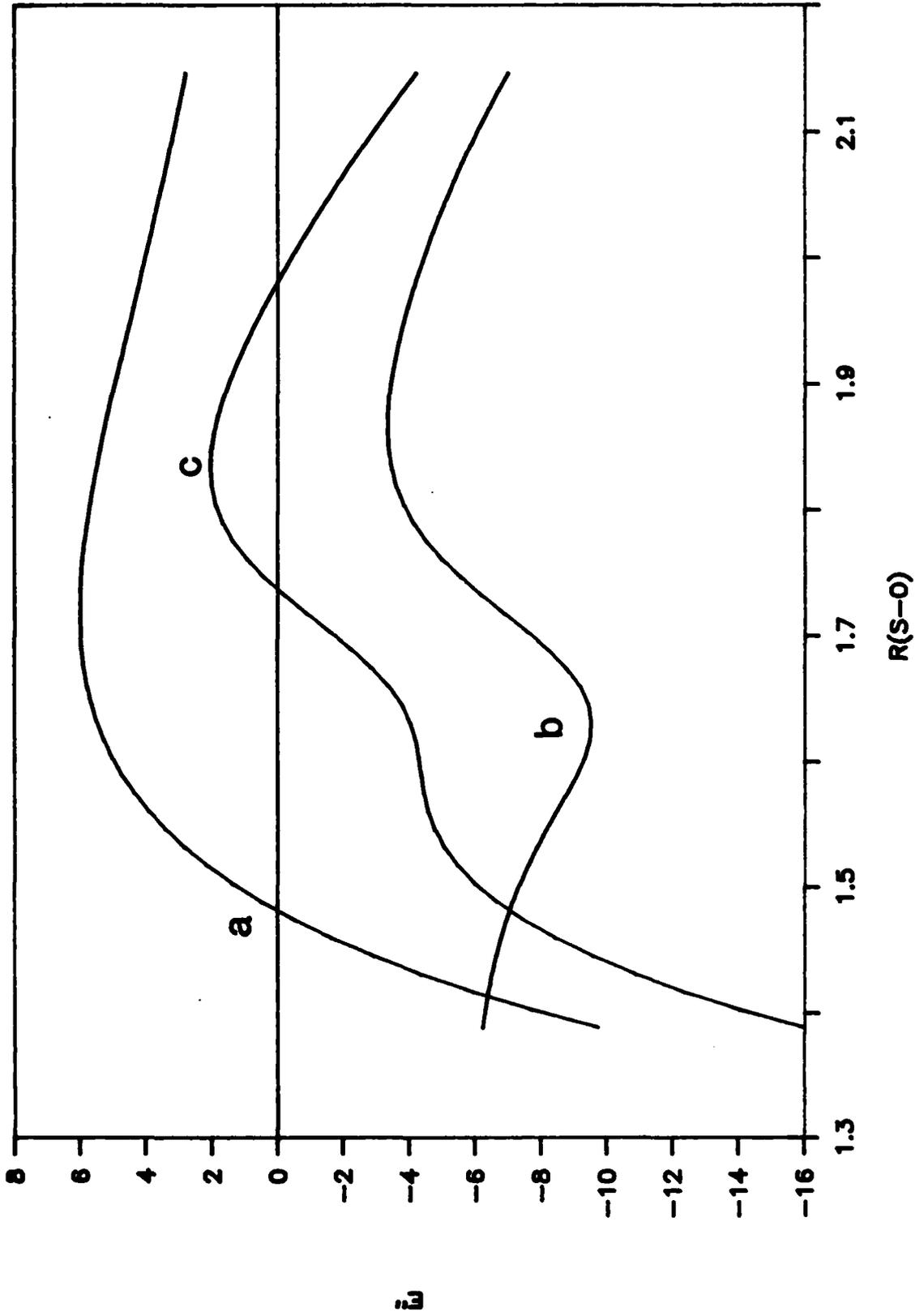
Axial reactive motion of S



Initial State

Transition state

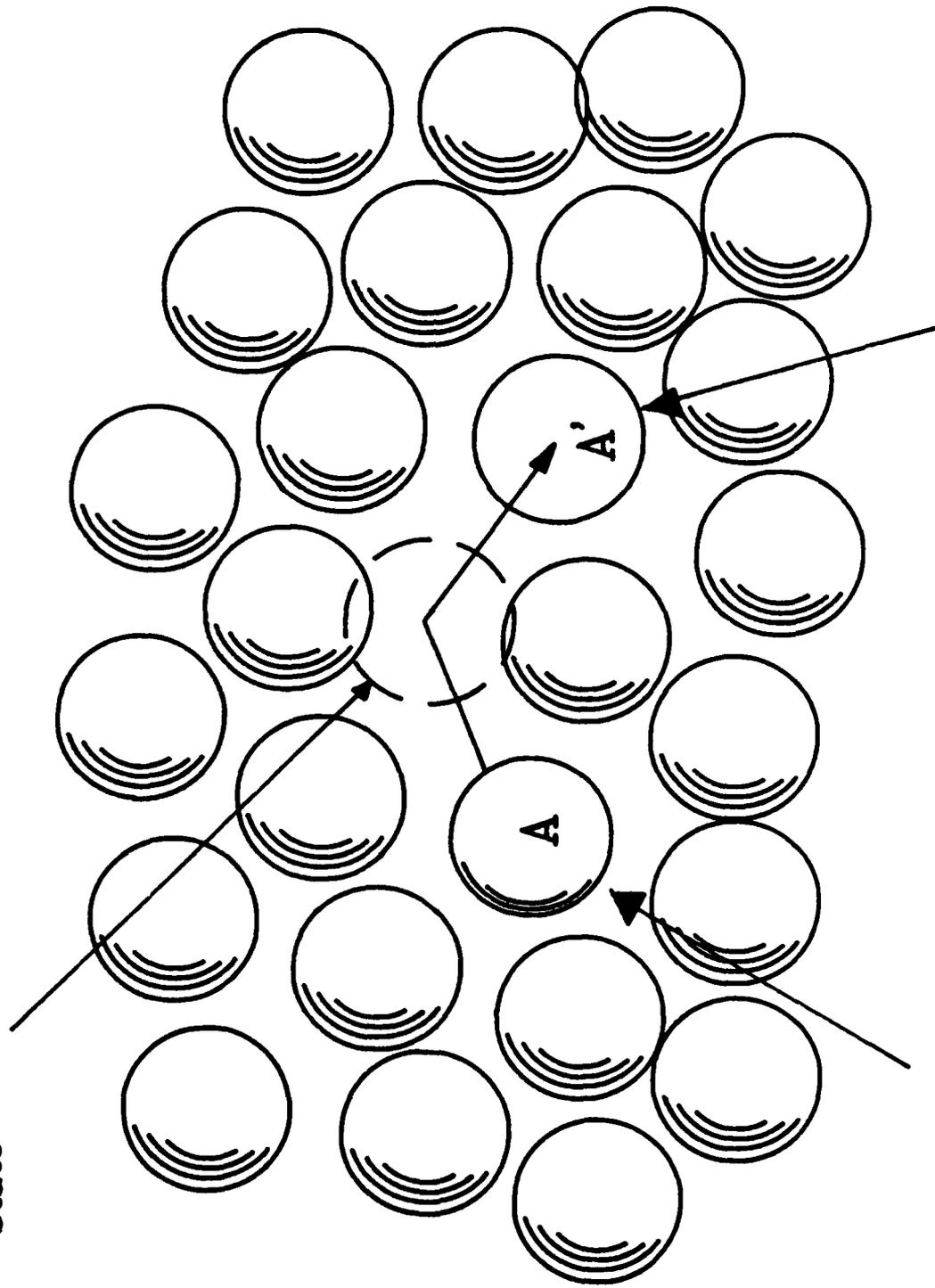




Oblique Transfer

Transition

State



Initial State

Final State

END

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DTIC