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# THE TRANSITION FROM NON-ADIABATIC TO SOLVENT CONTROLLED ADIABATIC ELECTRON TRANSFER: <br> SOLVENT DYNAMICAL EFFECTS IN THE INVERTED REGIME 

presented by

DAH-YEN YANG
has been accepted towards fulfillment
of the requirements for
Ph. D. degree in CHEMISTRY
$\qquad$


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# THE TRANSITION FROM NONADIABATIC TO SOLVENT CONTROLLED ADIABATIC ELECTRON TRANSFER: SOLVENT DYNAMICAL EFFECTS IN THE INVERTED REGIME 

By
Dah-Yen Yang

## A DISSERTATION

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## By

## DAB-YEN YANG

This study concerns the effect of solvent dynamics on non-adiabatic electron transfer reactions. A hamiltonian is designed to include: a reaction coordinate for two quadratic potential surfaces of donor and acceptor species and a heat bath which is characterized by a single Debye relaxation time $\tau_{L}$. Solvent dynamical effects are described by an indirect coupling between the reaction coordinate and the heat bath. The time evolution of this system is obtained by use of the quantum Liouville equation. After averaging over the solvent fluctuations, the dynamics along the reaction coordinate are reduced to a classical Fokker-Planck operator, but the motion of the electron is still treated quantum mechanically. When the rate of nuclear motion in the potential well is comparable to the non-adiabatic transition rate, a consecutive reaction scheme leads to a rate constant expression $\mathbf{k}_{12}=$ $k_{n a}^{T S T} k_{d}^{A r r} /\left(k_{n a}^{T S T}+k_{d}^{A r r}\right)$, the steps being the diffusion along the reaction coordinate with rate $k_{d}^{A r r}$ followed by crossing at the intersection of the donor and acceptor potential surfaces with a rate $k_{n a}^{\text {TST }} \cdot k_{d}^{A r r}$ is dependent on the solvent dynamical effects through $\tau_{L}$ and $k_{n a}^{\text {TST }}$ is independent of $\tau_{L}$. When the motion of the system in the
transition region must be treated quantum mechanically, the transition region can be spread out over a length larger than the mean free path. Then $k_{n a}^{\text {TST }}$ should be modified by solvent dynamic effects. When the separation into diffusive and crossing motion is no longer appropriate, we use an eigen-function method to expand the four coupled equations for the density matrix of the system, and solve for the reaction rate. A comparison of the numerical and analytical results is given.
ii

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## TABLE OF CONTENTS

LIST OF TABLES ..... $v$
LIST OF FIGURES ..... vi
LIST OF SYMBOLS ..... vii
CHAPTER I INTRODUCTION ..... 1
CHAPTER II DERIVATION OF EQUATIONS OF MOTION ..... 10
CHAPTER III ANALYTIC EXPRESSION FOR THE RATE CONSTANT ..... 22
CHAPTER IV NUMERICAL SOLUTION OF COUPLED EQUATIONS ..... 40
CHAPTER V RESULTS AND DISCUSSION ..... 48
APPENDIX A Formal derivation of reaction rate expression ..... 54
APPENDIX B Derivation of $\mathbf{G}_{12}$ ..... 59
APPENDIX C Eigen-function $\mathrm{L}_{12}$ ..... 64
APPENDIX D Vector recurrence relation ..... 68
REFERENCES ..... 74

## LIST OF TABLES

Table 1. Comparison of $k_{12}$ with $k_{n a}^{T S T}, k_{12}^{i r r}, k_{12}^{r e v}$. ..... 51
Table 2. Comparison of $\mathrm{k}_{12}$ with $\mathrm{k}_{12}^{\mathrm{ap}}$. ..... 52

## LIST OF FIGURES

## Figure 1. Potential energy surfaces for the reaction coordinate.

(a) Normal region (b) Activationless region
(c) Inverted region

Figure 2. Coordinate representation of the potential energy surfaces 14

Figure 3. Branching ratio diagram for the forward rate constant 24
Figure 4. Plot of $1 /\left(k_{d 1} \tau_{L}\right)$ versus $\beta \mathrm{Ea}$. ( - ) corresponds to $k_{d 1}$, ( ) corresponds to $k_{d r}^{A r r}$ 36
Figure 5. Plot of $k_{n a}^{12} \times 10^{-3}$ versus $\lambda$. $(\times)$ for $G_{12}$ in eq. (19.d), ( $)_{\text {) for }}^{G_{11}}$ in eq. (3.19d) 38

## LIST OF SYMBOLS

$a=4 \mathrm{~V}_{12} \tau_{\mathrm{L}} / \mathrm{h}$
$A=2 S /\left(\beta \boldsymbol{\hbar} \omega_{\mathbf{L}}\right)$
AA : frequency factor
$b=\lambda \sqrt{\mathbf{A}}$
$\mathrm{B}=\mathrm{S}-\mathrm{P}$
$\beta=1 / k_{B} T$
$c_{j}=\underline{L}_{\mathbf{j}}^{\mathbf{j}} \underline{\mathrm{V}}(0)$
$\chi=\left(1 / \lambda \tau_{L}\right)\left(\varepsilon_{0} / \varepsilon_{T}\right)^{3 / 4}$
$D_{1}, D_{2}$ : electric displacement of ion 1 and 2
$\Delta_{\alpha \beta}$ : overlap integral
D : diffusion constant
E. : activation energy

Er : reorganization energy
$\Delta E=V_{0}$ driving force
$\varepsilon_{\infty}$ : optical dielectric constant
$\varepsilon_{1}, \varepsilon_{2}$ : electron energy of the fast sub-system
$E_{1}, E_{2}$ : eigen-energy of reactant and product
$\Phi_{\alpha}(R)$ : wave function of slow (system or nuclei) variable
$\Phi_{1}, \Phi_{2}$ : pure state wave function of the system in state 1 and 2
$\Delta F$ : difference of the force at the crossing point
$\boldsymbol{\gamma}=\mathbf{k}_{\omega} \mathbf{x}_{\mathbf{0}}$ : slope at the crossing point
$G_{11}, G_{22}, G_{12}$ : Green function of $L_{11}, L_{22}, L_{12}$
E : distribution matrix

ћ : Planck constant
ऊ$\omega 1$ : phonon energy
$H_{n}$ : Hermite function
$\eta_{1}:$ rotation coordinate
$i=\sqrt{-1}$
I : unit matrix
$\mathbf{k}_{\mathrm{B}}$ : Boltzmann constant
$\mathbf{k}_{\mathrm{na}}^{\text {TST }}$ : non-adiabatic rate constant from Transition State Theory
$k_{n a}$ : non-adiabatic rate constant
$\mathbf{k}_{\mathbf{d}}$ : adiabatic rate constant
$k$ : reaction rate constant
$k_{12}^{i r}, k_{21}^{i r r}$ : irreversible rate constant
$k_{12}^{r e v}, k_{21}^{r e v}:$ reversible rate constant
$k_{A I}, k_{I_{A}}$ : reaction rate from $R A$ to $I$ and vice versa
$k_{B I}, k_{I B}$ : reaction rate from $P B$ to $I$ and vice versa
$\bar{x}_{r}, \bar{x}_{r}$ : rate kernel
$k_{12}, k_{21}$ : forward and backward reaction rate
K : reaction kernel
$k_{n a}^{12} k_{n a}^{21}$ : forward and backward non-adiabatic reaction rate
$\mathbf{k}_{d 1}, \mathbf{k}_{\mathrm{d} 2}$ : adiabatic reaction rate in potential well $R A$ and $P B$
$K_{n a}^{e q}$ : non-adiabatic equilibrium constant
$\mathbf{k}_{\mathbf{d r}}^{\text {Ar }}$ : Arrhenius adiabatic rate constant
$\mathbf{k}_{\omega}$ : force constant of the harmonic oscillator
$1_{T S}$ : the size of the transition region
$1_{f}$ : mean free path
$I_{\text {LZ }}$ : Landau-Zener length
$1=\left\langle x^{2}\right\rangle^{1 / 2}=k_{B} T / k_{\omega}$ : well motion length
$L_{11}, L_{22}, L_{12}, L_{21}:$ Fokker-Planck operator in potential surfaces $V_{11}$,

$$
v_{22}, \frac{1}{2}\left(v_{11}+v_{22}\right), \frac{1}{2}\left(v_{11}+v_{22}\right)
$$

$I_{n}$ : left hand side eigen-function of $L_{12}$
$\underline{L}_{j}, \underline{L}_{j}^{\prime}$ : left hand eigen-vector of $\underline{\underline{M}}$ and its conjugate
$\Lambda_{j}$ : eigen-value of $\underline{M}$
$\lambda=\tau_{\mathbf{L}} \omega_{\mathbf{L}}$
$\mu:$ delocalization width
$m_{\text {. }}$ : mass of electron
$\mu_{n}$ : eigen-value
$\mathrm{Na}, \mathrm{Nb}, \mathrm{Ni}$ : population in RA, PB, I
$\hat{\mathbf{N}}$ : Laplace transformation of $\underline{\mathbf{N}}$
PB : potential well of product
$\mathbf{P}^{\mathbf{L}}, \mathrm{P}^{\mathrm{T}}$ : longitudinal and transverse part of polarization
$Y\left(r, R, q_{k}\right)$ : wave function of the system
$\varphi_{\alpha}\left(r, q_{k}\right)$ : wave function for the fast variable
$P=\Delta E / h \omega_{L}$
$P_{i j}$ : Wigner representation of the probability distribution function
$\underline{\underline{P}}:$ : projection operátor
$P_{f}$ : transition probability from RA to $P B$
$P_{b}$ : transition probability to stay at PB
$Q_{\alpha \beta}:$ non-adiabaticity operator
Q : complement of projection operator $\underline{\underline{P}}$
RA : potential well of reactant
$\underline{\varrho}$ : density matrix
$\underline{\rho}$ : reduced density matrix
$\hat{\rho}$ : Laplace transform of $\underline{\rho}$
$\underline{R}_{j}$ : right hand side eigen-vector of $\underline{M}$
$\mathbf{R}_{1,0}$ : components of $\underline{R}_{0}$
$r_{n}$ : right hand side eigen-function of $L_{12}$
$\sigma$ : position of crossing point
$\sigma_{y}=\sigma-\frac{1}{2} x_{0}$
S:Er/h $\omega_{L}$
T : temperature
$\tau_{D}, \tau_{l}$ : transverse and longitudinal relaxation time
$\bar{t}=t / r_{L}$
$\tau=\mathbf{k}_{12}+\mathbf{k}_{21}$
$V_{11}$ : potential surface of reactant $R A$
$V_{22}$ : potential surface of product PB
$\mathrm{V}_{12}$ : electronic coupling constant
$\mathrm{V}_{\mathrm{o}}$ : driving force
$\omega_{L}=\sqrt{k_{\omega} / \bar{m}_{L}}$
$\mathrm{x}_{0}$ : minimum point of PB
$x^{*}=\sigma / \sqrt{\beta k_{\omega}}$

## I. INTRODUCTION

In oxidative
phosphorylation,
photosynthesis,
and oxidation-reduction reactions, electron transfer (ET) is an important chemical process. Non-adiabatic transitions may occur in long-ranged ET or the spin change of reactants. Recently, Kosower and co-workers ${ }^{1}$ have found that ET rates in polar aliphatic alcohols are inversely proportional to the slowest dielectric relaxation time $\tau_{L^{*}}$. This showe that the solvent dynamic effects can influence non-adiabatic ET, which has attracted considerable attention.

The pioneering work of Marcus ${ }^{2}$ showed that, in the high-temperature regime, the ET rate has the thermally activated Arrhenius form $k_{n a}^{T S T}=A A \exp \left(-B a / k_{B} T\right)$. The activation energy is the height of the nuclear barrier $E a=(\Delta E-E r)^{2} / 4 \mathrm{Er}$. This expression for the activation energy is valid in the classical limit when quantum effects of nuclear tunneling are omitted. In Marcus' work, the ET process is adiabatic. Levich ${ }^{3}$ has treated ET as a non-adiabatic process using the Fermi-Golden rule rate expression. The medium is modeled by a set of harmonic oscillators. The frequency factor in the classical limit is $A A=(2 \pi / \hbar) \quad V_{12}^{2}\left(4 \pi \quad E r \quad k_{B}\right)^{-1 / 2}$. Zusman analysed ${ }^{4}$ the situation when the dynamics of the reaction coordinate is diffusive rather than uniform; his approach rests upon the stochastic Liouville equation. In the extreme adiabatic limit, when the dynamics of the
reaction coordinate reduces to diffusion over the low adiabatic surface, Zusman's expression reduces to Kramers' result ${ }^{5}$. Zusman's result also connects the non-adiabatic limit for the frequency factor, which is determined by the electronic coupling, and the solvent-controlled adiabatic limit, which is determined by the reaction coordinate dynamics. In the non-adiabatic limit, the frequency factor is AA, while in the solvent-controlled adiabatic limit the frequency factor is proportional to $\tau_{L}^{-1}$.

The most popular harmonic oscillator model is composed of two quadratic potential surfaces which cross, embedded in a polar mediated heat bath. When the system is at equilibrium, before the electron is transferred, the system is located at the minimum of potential well RA (see figure 1). When the solvent fluctuates (the system deviates from the equilibrium state), the system will move away from the minimum point. This deviation from the equilibrium state, which is activated by thermal energy, is described by a coordinate called the reaction coordinate. Since the dipole moment of the solvent always fluctuates due to thermal energy, and this may be described by diffusive motion, the system will diffuse along the potential surface. The splitting at the crossing point of the two surfaces is $2 \mathrm{~V}_{12}$ (from the point of view of the adiabatic representation). When $2 V_{12}>k_{B} T$, the system with thermal energy can not jump to the upper surface. The system will transfer from the left minimum to the right minimum within the same surface. This is called an adiabatic transition. When $2 V_{12}<k_{B} T$, the system get enough thermal energy to jump to the upper surface several times before crossing. This is called a non-adiabatic transition. The
analysis of the relation between non-adiabatic and adiabatic ET is important for the understanding of solvent dynamic effects. We first summarize the outstanding problems ${ }^{6}$ as follows: 1) the relation between the ET dynamics along the reaction coordinate and the dissipation of the medium. Frauenfelder and Wolynes ${ }^{7}$ have considered the relationship between the mean free path and the Landau-Zener length. They get two limiting physical situations: uniform dynamics and diffusive dynamics. 2) The relation between the ET dynamics and the strength of the electronic coupling. This depends on the distinction between the strong and weak electronic coupling in the Landau-Zener transition, which is determined by the $L Z$ parameter $I_{L Z^{\circ}}$. These two $L Z$ limits are the non-adiabatic and adiabatic coupling limits. 3) The nature of the dissipative properties of the medium and of the strength of the electronic coupling. The interesting physical situtations are: non-adiabatic ET, solvent controlled adiabatic ET, and uniform-adiabatic ET. 4) The transition between non-adiabatic and the solvent controlled adiabatic ET. 5) The competition between ET and medium relaxation. The basic implicit assumption of general non-adiabatic ET theory includes the separation of the time scales for the fast medium dielectric relaxation and for the slow electronic processes. When the microscopic ET rates of a given state are comparable to the medium relaxation rates, the ET process is expected to be determined by the longitudinal dielectric relaxation time $\tau_{\mathbf{L}}$ corresponding to the solvent controlled adiabatic limit.

These two quadratic potential surfaces have three different combinations: normal, activationless, and inverted regimes. In the


Figure 1a. Potential energy surfaces for the reaction coordinate. Normal region
ENERGY

$x$

Figure 1b. Potential energy surfaces for the reaction coordinate. Activationless region


$$
x
$$

Figure 1c. Potential energy surfaces for the reaction coordinate. Inverted region
normal regime, with barrier energy larger than $k_{B} T$, the non-adiabatic transition rate is $\left.k_{n a}^{T S T}=\frac{\beta V \frac{2}{2}}{2} \frac{\pi}{\beta E a}\right)^{1 / 2} \exp (-\beta$ Ea). This is the Arrhenius law which describes localized transitions and $k_{n a}^{\text {TST }}$ is independent of $\tau_{i}$. The diffusion motion inside the potential surface gives $k_{d r}^{A r r}=\frac{1}{\tau_{L}}\left(\frac{\beta E a}{\pi}\right)^{1 / 2} \exp (-\beta E a)$, which depends on $\tau_{L}$. Both $k_{n a}^{\text {TST }}$ and $k_{d}^{\text {Arr }}$ include an exponential part and a prefactor. For $k_{n=}^{\text {TST, }}$ the prefactor is proportional to the aquare of $V_{12^{\circ}}$ Usually this makes $k_{n a}^{\text {TST }}$ much smaller than $k_{d}^{A r r}$. In the activationless or low barrier energy regime, it is still not clear how to describe the transition rate. The inverted regime which has been discussed by Marcus ${ }^{8}$ has strong quantum behavior. The region that nuclei can tunnel through is called the delocalization width $\mu^{9}$ (see figure 1c). When $\mu$ is spread out this means that the system exhibts strong quantum behavior. The diffusive motion inside the tunneling region is our main topic in this work.

Rips and Jortner ${ }^{6}$ studied the reaction rate by using a path integral formalism that ultimately reduces to a consecutive mechanism. This method separates the reaction rate into diffusive and reactive part. The total rate is $1 / k_{12}=1 / k_{d}^{A r r}+1 / k_{n a}^{\text {TST }}$. When $k_{d}^{A r r}$ \# $k_{n a}^{T S T}, k_{12}=k_{n a}^{\text {TST }}$; the rate constant for the rate determining step is $k_{n a}^{\text {TST }}$ which is independent of $\tau_{i}$. If we increase the friction of the solvent, $\tau_{l}$ is increased and $k_{d}^{A r r}$ is decreased, to make $k_{d r}^{A r r}<k_{n a}^{T S T}$; then $k_{12}=k_{d}^{A r}$. The rate constant for the rate determining step is $k_{d}^{A r r}$. The solvent effect (through the longitudinal dielectric relaxation time $\tau_{L}$ ) makes the transition rate slow down and the rate
constant $k_{12}$ is changed from the non-adiabatic transition rate $k_{n a}^{\text {TST }}$ to the adiabatic transition rate $\mathbf{k}_{\mathrm{d}}^{\mathrm{Ar}}$. This shows how the solvent can controll the transition rate from non-adiabatic to adiabatic behavior (for an adiabatic transition, the reaction rate is independent of the electronic coupling $V_{12}$ ). In the work of Rips and Jortner, $k_{n a}^{\text {TST }}$ is independent of $\tau_{1}$, and the delocalization width $\mu<\eta_{f}$ Morillo and Cukier ${ }^{10}$ showed, with $1 \geqslant$ the delocalization width $\mu \geqslant I_{f}$, that $k_{n a}^{12}=$ $\frac{\mathrm{V} 12(\pi / \mathrm{Er} \mathrm{kBT})^{1 / 2}}{1+X} \exp \left(-\frac{(\mathrm{Er}-1 \mathrm{E} \mid)^{2}}{4 \operatorname{Er} \mathrm{k}_{\mathrm{B}} \mathrm{C}} \frac{1}{1+\chi}\right)$. Here $\mathrm{k}_{\mathrm{na}}^{12}$ depends on $\tau_{L}$. The situation that we are going to study is when $1 \approx \mu \geqslant \mathcal{I}_{f}$; what is the reaction rate expression? And will the consecutive mechanism still be sensible?

In this work ${ }^{20}$, a Debye solvent has been used. The dielectric fluctuation has frequency lower than $k_{B} T / h$. A classical diffusive motion of the system along the potential surfaces can simplify the calculation. The tunneling effect still needs to be kept in a quantum manner. The problem is formulated by using a density matrix in Liouville space. By use of the Wigner transformation, a set of semi-classical Zusman equations has been obtained, which were written down by Zusman without derivation. By averaging over all the solvent degrees of freedom excluding the reaction coordinate, a classical Fokker-Planck operator is obtained to describe the diffusive motion of the system. The quantum transition is kept in the off-diagonal terms. So, we have a set of semi-classical equations of motion. A phenomenological rate constant is defined ${ }^{11}$. To calculate the Laplace transformed rate kernel, an appropriate truncation of the Zusman
equations with reasonable assumptions gives us two reduced coupled equations. The well-known projection operator method ${ }^{12}$ is used to separate equilibrium and non-equilibrium parts of the motion. $A$ consecutive mechanism can be sucessfully introduced to separate diffusive and reactive dynamics. The final rate expression interpolates between the adiabatic and the solvent-controlled non-adiabatic limits. The effects of the solvent on the adiabatic character are clarified. A careful study of the non-adiabatic transition rate shows the solvent dynamic effects in it. We show that, in the inverted regime, friction makes the quantum behavior more classical. Beyond the regime that the consecutive mechanism can be used, an exact numerical calculation has been done. An eigen-function expansion method ${ }^{13}$ transforms our equations of motion into four coupled first order differential equations. The total reaction rate can be identified with the smallest non-zero eigenvalue ${ }^{14}$. With large fluctuations included, a vector continued fraction method has been used to extract a relatively small eigen-value.

The model hamiltonian for the rate process in condensed phases will be introduced in chapter II. In chapter III, we define the rate expression and truncate the Zusman equations. The projection operator method is used to get the final rate constant expression. We also analyze the non-adiabatic rate constant in detail. The numerical calculations will be described in chapter IV. The results of numerical calculations and discussion of the validity of our consecutive mechanism are given in chapter V .

## II. DERIVATION OF EQUATION OF MOTION

The electron transfer problem consists of a transfer of an electron from one localized state $R A\left(D^{-} A\right)$ to another localized state $\mathrm{PB}\left(\mathrm{DA}^{-}\right)$within the same molecule or between different molecules. We shall consider Levich's model ${ }^{3}$ in our following study to derive a quantum mechanical hamiltonian. The model consists of electron + donor + acceptor + solvent. Donor and acceptor carry charge $n+$ and $m+$, and there is no first coordination layer of the ions in Levich's model. The solvent is a continuum polar medium which is characterized by the polarization $P(r, t)$ of the optical vibrational branch of the solvent. A polaron model of this polarization has been used, so the solvent consists of a set of phonons. The total hamiltonian of the system is $\mathrm{H}=\mathrm{H}_{\mathrm{e}}+\mathrm{H}_{\mathrm{e}}+\mathrm{V}_{\mathrm{ie}}+\mathrm{V}_{\bullet \mathrm{e}} \quad$ (2.1) where

$$
\begin{align*}
& H_{z}=\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left(q_{k}^{2}-\frac{\partial^{2}}{\partial q_{k}^{2}}\right)+\frac{\varepsilon_{\infty}^{2}-1}{8 \pi \varepsilon_{\infty}^{2}} \int\left(D_{1}^{2}+D_{2}^{2}\right) d V  \tag{2.2}\\
& H_{e}=-\frac{h^{2}}{2} \frac{\nabla^{2}}{} e^{2}+\frac{n e^{2}}{r}+\frac{m e^{2}}{T r} \frac{e^{2} T}{} \\
& V_{1 e}=-m e \int \frac{\operatorname{div} P\left(r^{\prime}\right)}{\left|R-r^{\prime}\right|} d V-n e \int \frac{\operatorname{div} P\left(r^{\prime}\right)}{\left|r^{\prime}\right|} d V \\
& v_{e s}=-e \int \frac{\operatorname{div} P\left(r^{\prime}\right)}{\left|r-r^{\prime}\right|} d V  \tag{2.5}\\
& \varepsilon_{\infty} \text { is the optical dielectric constant. }
\end{align*}
$$

$H_{\text {s }}$ describes the energy of the solvent: the first term is the energy of phonons which is described by the normal coordinates $q_{k}$, and the second term is the energy of the solvent which is produced by the electric displacement $D_{1}$ and $D_{2}$ due to the ions. $H_{0}$ is the energy of the electron where the donor and acceptor are located at position 0 and R. $V_{i s}$ is the coupling between ions and solvent. $V_{e s}$ is the coupling between electron and solvent. If we decompose $P$ into $P=P^{\mathbf{L}}+P^{T}$, from $\operatorname{div} P^{T}=0$, we can see that only the longitudinal part of $P$ will contribute to $V_{i,}$ and $V_{e e^{\circ}}$ This is important in our choosing the relaxation time of the solvent. The Schrodinger equation is
$H \Psi\left(r, R, q_{k}\right)=E \Psi\left(r, R, q_{k}\right)$.

In order to solve the Schrodinger equation, we can use the Born-Oppenheimer approximation to separate out the fast and slow motion of the system, which comes from the fact that both the fast motion of electron and the slow motion of heavy solvent particles are included in the total hamiltonian. Let

$$
\begin{equation*}
\Psi\left(r, R, q_{k}\right)=\sum_{\alpha=1,2} \phi_{\alpha}(R) \psi_{\alpha}\left(r, q_{k}\right) \tag{2.7}
\end{equation*}
$$

and let $\psi_{\alpha}\left(r, q_{k}\right)$ satisfy

$$
\begin{align*}
& {\left[-\frac{\hbar^{2}}{2} \frac{\nabla_{e}}{e} \nabla_{e}^{2}+u_{1}+v_{e s}+v_{i s}+\frac{\varepsilon_{\infty}^{2}-1}{8 \pi \varepsilon_{\infty}^{2}} \int\left(D_{1}^{2}+D_{2}^{2}\right) d V\right] \psi_{1}} \\
& =\varepsilon_{1} \Psi_{1}  \tag{2.8}\\
& {\left[-\frac{\hbar^{2}}{2 m} \nabla_{\bullet}^{2}+u_{2}+v_{e s}+v_{i s}+\frac{\varepsilon_{\infty}^{2}-1}{8 \pi \varepsilon_{\infty}^{2}} \int\left(D_{1}^{2}+D_{2}^{2}\right) d V\right] \psi_{2}}
\end{align*}
$$

$$
\begin{equation*}
=\varepsilon_{2} \Psi_{2} \tag{2.9}
\end{equation*}
$$

where
$u_{1}=\frac{n \theta^{2}}{r}+\frac{m e^{2}}{r-R T}$
$u_{2}=\frac{m e^{2}}{r}+\frac{n e^{2}}{-R T}$.

Substituting into the Schrödinger equation and multiplying with $\psi^{*}$, then integrating over the volume, we get
$\left[H_{8}+\varepsilon_{1}-E_{1}\right] \Phi_{1}=V_{12} \Phi_{2}$
$\left[H_{8}+\varepsilon_{2}-E_{2}\right] \Phi_{2}=V_{21} \Phi_{1}$
where

$$
\begin{align*}
& V_{12}=Q_{12}-\Delta_{12}\left(H_{s}+\varepsilon_{2}-E\right)  \tag{2.14}\\
& V_{21}=Q_{21}-\Delta_{12}\left(H_{s}+\varepsilon_{1}-E\right) \tag{2.13}
\end{align*}
$$

$\Delta_{\alpha \beta}= \begin{cases}0 \\ \int \Psi_{\alpha}^{*} \Psi_{\beta} d V & , \alpha=\beta \\ \alpha \neq \beta\end{cases}$
$Q_{\alpha \beta}=\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left[\left(\int \psi_{\alpha}^{*} \frac{\partial}{\partial q_{k}} \psi_{\beta} d V\right)\left(\frac{\partial}{\partial q_{k}}\right)+\int \varphi_{\alpha}^{*} \frac{\partial^{2} \varphi_{\beta}}{\partial q_{k}^{2}} d V\right.$

$$
\begin{equation*}
\left.+\int \psi_{\alpha}^{*} u_{\beta} \psi_{\beta} d v\right] \tag{2.15}
\end{equation*}
$$

This describes the Born-Oppenheimer states $\Phi_{1}$ and $\Phi_{2}$ of the system in initial and final state. The displacement of the heavy molecules of solvent caused by the electric field of the electron is small and a linear approximation of $\varepsilon_{\alpha}\left(q_{k}\right)$ relative to the equilibrium state can
be used. So
$\varepsilon_{\alpha}\left(q_{k}\right)=\varepsilon_{\alpha}\left(q_{k}^{(0)}\right)+\sum_{k=1}^{\infty}\left(\frac{\partial \varepsilon_{\alpha}}{\partial q_{k}}\right)_{q_{k}=} q_{k}^{(0)}\left(q_{k}-q_{k}^{(0)}\right),(2.16)$
where $q_{k}^{(0)}$ is the equilibrium position of $q_{k}$. Now the total hamiltonian is

$$
H_{s}+\varepsilon_{\alpha}=\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left\{\left(q_{k}-q_{k}^{(0)}\right)^{2}-\frac{\partial^{2}}{\partial\left(q_{k}-q_{k}^{(0)}\right)^{2}}\right\}+T_{\alpha},
$$

where

$$
\mathrm{T}_{\alpha}=\varepsilon_{\alpha}\left(q_{k}^{(0)}\right)+\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left(q_{k}^{(0)}\right)^{2} ;
$$

i.e.

$$
\begin{aligned}
& H_{1}=\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left\{\left(q_{k}-q_{k 1}^{(0)}\right)^{2}-\frac{\partial^{2}}{\partial\left(q_{k}-q_{k 1}^{(0)}\right)^{2}}\right\}+T_{1} \quad(2 \cdot 19 a) \\
& H_{2}=\frac{\hbar \omega_{1}}{2} \sum_{k=2}^{\infty}\left\{\left(q_{k}-q_{k 2}^{(0)}\right)^{2}-\frac{\partial^{2}}{\partial\left(q_{k}-q_{k 2}^{(0)}\right)^{2}}\right\}+T_{2} .(2 \cdot 19 b)
\end{aligned}
$$

If we set

$$
\begin{equation*}
\xi_{k}=q_{k}-q_{k 1}^{(0)} \tag{2.20}
\end{equation*}
$$

and

$$
\begin{equation*}
\xi_{k}^{(0)}=q_{k}^{(0)}-q_{k 1}^{(0)} \tag{2.21}
\end{equation*}
$$



Figure 2. Coordinate representation of the potential energy surface.
then

$$
H_{1}=\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left(\xi_{k}^{2}-\frac{\partial^{2}}{\partial \xi_{k}^{2}}\right)+T_{1}
$$

$H_{2}=\frac{\hbar \omega_{1}}{2} \sum_{k=1}^{\infty}\left[\left(\xi_{k}-\xi_{k}^{(0)}\right)^{2}-\frac{\partial^{2}}{\partial \xi_{k}^{2}}\right]+T_{2}$.

Since $q_{k}$ is the normal mode of the vibration, $\xi_{k}$ can be thought of as another N orthogonal coordinates in $\xi$-space. With a rotation of the coordinate $\xi_{k}$, a new coordinate set $\eta_{1}=\sum_{k} \alpha_{i k} \xi_{k}$ is obtained. After the rotation of the coordinate $\xi_{k}$, the potential energy hypersurface of $H_{2}$ is on axis $\eta_{1}$ (see figure 2). The final hamiltonians are

$$
\begin{align*}
& H_{1}=\frac{\hbar \omega_{1}}{2} \sum_{k=2}^{\infty}\left(\eta_{k}^{2}-\frac{\partial^{2}}{\partial{\eta_{k}^{2}}^{2}}\right)+\frac{\hbar \omega_{1}}{2}\left(\eta_{1}^{2}-\frac{\partial^{2}}{\partial \eta_{1}^{2}}\right)+T_{1}(2 \cdot 23 a) \\
& H_{2}=\frac{\hbar \omega_{1}}{2} \sum_{k=2}^{\infty}\left(\eta_{k}^{2}-\frac{\partial^{2}}{\partial \eta_{k}^{2}}\right)+\frac{\hbar \omega_{1}}{2}\left[\left(\eta_{1}-\eta_{0}\right)^{2}-\frac{\partial^{2}}{\partial \eta_{1}^{2}}\right]+T_{2}
\end{align*}
$$

where

$$
\begin{equation*}
\eta_{0}^{2}=\sum_{k=1}^{\infty}\left(\xi_{k}^{(0)}\right)^{2} \tag{2.24}
\end{equation*}
$$

The $\eta_{1}$ axis can be thought of as the reaction coordinate; the other N-1 dimensions are the same for $H_{1}$ and $H_{2}$, and can be thought of as solvent coordinates. Unfortunately, there is no coupling between reaction and solvent coordinates from this perspective. It is not clear how to
derive the coupling rigorously from a hamiltonian model. We will put the coupling term (between reaction and solvent coordinate) into the hamiltonian artificially (see eq. (2.25)).

In the following, we will assume that the system moves on one dimensional potential surfaces (or reaction coordinate) which are BornOppenheimer surfaces. There are two well-separated minima which correspond to $\mathrm{D}^{-} \mathrm{A}$ and $\mathrm{DA}^{-}$. The heat bath will couple dynamically to the motion of the system. So the motion of the system on the reaction coordinate is described by the quantum Liouville equations. Using the Wigner transformation, four classical-like equations are obtained. We use classical Fokker-Planck operators to describe nuclear (solvent polarization) motion, and the electronic coupling is still kept in a quantum manner.

The hamiltonian is

$$
\begin{equation*}
H=H_{0} \hat{\sigma}_{0}+\frac{1}{2}\left(v_{11}-v_{22}\right) \hat{\sigma}_{z}+V_{12} \hat{\sigma}_{x}, \tag{2.25}
\end{equation*}
$$

where

$$
\begin{align*}
H_{0}= & {\left[-\sum_{\alpha} \frac{\hbar^{2}}{2} \frac{\nabla_{\alpha}}{2}+V\left(\left(q_{k}\right\}\right)\right]+\left[-\frac{\hbar^{2}}{2 \mu} \nabla_{x}^{2}+\frac{1}{2}\left(v_{11}+v_{22}\right)\right] } \\
& +V\left(\left(q_{k}\right\}, x\right), \tag{2.26}
\end{align*}
$$

and

$$
\hat{\sigma}_{0}=\left[\begin{array}{ll}
1 & 0 \\
0 & 1
\end{array}\right], \quad \hat{\sigma}_{x}=\left[\begin{array}{ll}
0 & 1 \\
1 & 0
\end{array}\right], \quad \hat{\sigma}_{z}=\left[\begin{array}{rr}
1 & 0 \\
0 & -1
\end{array}\right]
$$

are Pauli spin matrices.

In $H_{0}$, the first term is the heat bath hamiltonian, the second term is the motion of the system on reaction coordinate, $V\left(\left\{q_{\alpha}\right\}, x\right)$ is the coupling between the reaction coordinate and the heat bath. We assume there are no off-diagonal terms in $\mathrm{V}\left(\left\{q_{\alpha}\right\}, \mathrm{x}\right)$ i.e.

$$
v_{12}\left(\left\{q_{\alpha}\right\}, x\right)=v_{21}\left(\left\{q_{\alpha}\right\}, x\right)=0 \quad(2 \cdot 27)
$$

and

$$
\begin{align*}
v_{11}\left(\left\{q_{k}\right\}, x\right) & =v_{22}\left(\left\{q_{k}\right\}, x\right) \\
& =v\left(\left\{q_{k}\right\}, x\right) \tag{2.28}
\end{align*}
$$

The two-level pure state wave function is $\Phi=\Phi_{1}\left(\left\{q_{k}\right\}, x\right)+\phi_{2}\left(\left\{q_{k}\right\}, x\right)$, so the density matrix $\underset{=}{\rho}=\Phi \Phi^{*}$. The Schrödinger equation of our system is

$$
\begin{equation*}
i \hbar \frac{\partial}{\partial t} \underset{=}{\rho}=[H, \rho] \tag{2.29}
\end{equation*}
$$

Its components' forms are

$$
\begin{align*}
& i \hbar \frac{\partial}{\partial t} \phi_{1} \phi_{1}^{*}=\left[H_{0}, \phi_{1} \phi_{1}^{*}\right]+\left[\frac{1}{2}\left(v_{11}-v_{22}\right), \phi_{1} \phi_{1}^{*}\right] \\
& +\left[v_{12} \phi_{2} \phi_{1}^{*}-\phi_{1} \phi_{2}^{*} v_{12}\right] \\
& i \hbar \frac{\partial}{\partial \mathrm{t}} \phi_{1} \phi_{2}^{*}=\left[\mathrm{H}_{0}, \phi_{1} \phi_{2}^{*}\right]+\left\{\frac{1}{2}\left(\mathrm{v}_{11}-\mathrm{V}_{22}\right), \phi_{1} \phi_{2}^{*}\right\} \\
& +\left[v_{12} \phi_{2} \phi_{2}^{*}-\phi_{1} \phi_{1}^{*} v_{12}\right]
\end{align*}
$$

$$
\begin{aligned}
& i \hbar \frac{\partial}{\partial t} \phi_{2} \phi_{1}^{*}=\left[H_{0}, \phi_{2} \Phi_{1}^{*}\right]-\left\{\frac{1}{2}\left(\mathrm{v}_{11}-\mathrm{V}_{22}\right), \phi_{2} \phi_{1}^{*}\right\} \\
& +\left[v_{12} \phi_{1} \phi_{1}^{*}-\phi_{2} \phi_{2}^{*} v_{12}\right] \\
& \text { (2.30c) } \\
& i \hbar \frac{\partial}{\partial t} \phi_{2} \phi_{2}^{*}=\left[H_{0}, \phi_{2} \phi_{2}^{*}\right]-\left[\frac{1}{2}\left(v_{11}-v_{22}\right), \phi_{2} \phi_{2}^{*}\right] \\
& +\left[v_{12} \Phi_{1} \phi_{2}^{*}-\phi_{2} \phi_{1}^{*} v_{12}\right] . \\
& \text { ( } 2 \text {. 30d ) }
\end{aligned}
$$

Two kinds of terms appear: commutator and anti-commutator. A non-adiabatic transition is a quantum transition, so we must start from a quantum description. But we want to treat the solvent classically. For a quantum system, especially a quantum statistical mechanical system, the Wigner transformation ${ }^{15}$ gives an appropriate procedure to transform from quantum to classical motion, because a Poisson bracket-like term which describes a Liouville equation is obtained and this describes classical motion.

The Wigner transformation is defined by

$$
\begin{align*}
P_{i j}= & \left.(\pi \hbar)^{-(N+1}\right) \int d y d\left\{y_{\alpha}\right\} \exp \left\{\frac{2}{\hbar}\left(p y+p_{\alpha} y_{\alpha}\right)\right\} \\
& \phi_{i}\left(x-y, q_{\alpha}^{N}-y_{\alpha}^{N}\right) \phi_{j}^{*}\left(x+y, q_{\alpha}^{N}+y_{\alpha}^{N}\right) \tag{2.31}
\end{align*}
$$

We simplify the expression to one degree of freedom only. The commutator part is

$$
\begin{aligned}
& {\left[-\frac{\hbar^{2}}{2} \frac{m}{2}+V, \phi_{i} \Phi_{j}^{*}\right] } \\
= & (\pi \hbar)^{-1} \int d y e^{\frac{21}{\hbar} p y}\left[-\frac{\hbar^{2}}{2} \nabla^{2}+V, \Phi_{i}(x-y) \phi_{j}^{*}(x+y)\right]
\end{aligned}
$$

$=i h\left\{-\frac{p}{m} \frac{\partial}{\partial x}, P_{i j}\right\}_{P . B .}+2 i \sin \left[\frac{h}{2} \nabla_{x} \nabla_{p}\right] V P_{i j}$.

The Poisson bracket term is similiar to a Liouville equation classically. The sine term can be expanded by using a Taylor expansion and the lowest order term can be included in the Poisson bracket term. The higher order terms which include $\hbar^{n}\binom{n}{2}$ describe the quantum correction, and are not of interest here.

The anti-commutator is

$$
\begin{align*}
& \left\{V, \phi_{i} \phi_{j}\right\}=(\pi \hbar)^{-1} \int e^{\frac{2 i}{\hbar} p y}\left\{V, \phi_{i}(x-y) \phi_{j}(x+y)\right\} \\
& =2 \cos \left[\frac{\hbar}{2} \nabla_{x} \nabla_{p}\right] V P_{i j} . \tag{2.34}
\end{align*}
$$

We want to treat the solvent classically, so higher order terms of the Taylor expansion of the cosine term are omitted too. The Liouville equation that we obtained yields the Fokker-Planck operator, following the well-known procedure (see ref. 16). Let
$\rho_{i j}=\int d p P_{i j}$,
then we have

$$
\begin{align*}
& \frac{\partial}{\partial t} \rho_{11}=L_{11} \rho_{11}+\frac{V}{i \hbar}\left(\rho_{21}-\rho_{12}\right) \\
& \frac{\partial}{\partial t} \rho_{22}=L_{22} \rho_{22}+\frac{V_{12}}{i \hbar}\left(\rho_{12}-\rho_{21}\right)
\end{align*}
$$

$$
\begin{aligned}
& \frac{\partial}{\partial t} \rho_{12}=L_{12} \rho_{12}+\frac{\left(V_{11}-V_{22}\right)}{i \hbar} \rho_{12}+\frac{V_{12}}{i \hbar}\left(\rho_{22}-\rho_{11}\right)(2.36 c) \\
& \frac{\partial}{\partial t} \rho_{21}=L_{21} \rho_{21}-\frac{\left(V_{11}-V_{22}\right)}{i \hbar} \rho_{21}+\frac{V_{12}}{i \hbar}\left(\rho_{11}-\rho_{22}\right)(2.36 d)
\end{aligned}
$$

The potential surfaces in $L_{i j}$ are, from equation (1-4): $\left(V_{11}\right.$ $\left.+\mathrm{V}_{22}\right) / 2+\left(\mathrm{V}_{11}-\mathrm{V}_{22}\right) / 2=\mathrm{v}_{11},\left(\mathrm{v}_{11}+\mathrm{V}_{22}\right) / 2,\left(\mathrm{v}_{11}+\mathrm{V}_{22}\right)$ $/ 2,\left(\mathrm{~V}_{11}+\mathrm{V}_{22}\right) / 2-\left(\mathrm{V}_{11}-\mathrm{V}_{22}\right) / 2=\mathrm{V}_{22}$ in $\mathrm{L}_{11}, \mathrm{~L}_{12} \mathrm{~L}_{21}, \mathrm{~L}_{22}$ where $L_{i j}$ are the Fokker-Planck operators.

The motion of the system in the initial and final potentials ( $V_{11}$ and $V_{22}$ ) is determined explicitly, and the off-diagonal terms are described by the motion on the averaged potential surfaces.

These semi-classical equations describe the solvent dielectric fluctuation as a low frequency fluctuation with energy amaller than $k_{B} T$. So the solvent is treated classically. The relaxation time in the Fokker-Planck operator is $\tau_{L}$ (longitudinal relaxation time) instead of $\tau_{\mathrm{D}}$ (transverse relaxation time), because only the longitudinal part of the solvent polarization contributes to the interaction with electrons (see eq. (2.1c,d)). Recently, many investigators ${ }^{17}$ have claimed the relaxation time should have an order of magnitude between $\tau_{L}$ and $\tau_{D}$ (usually $\tau_{D}>\boldsymbol{\tau}_{L}$ ). In our model, a continuum medium has been used, so the relaxation time is fixed at $\tau_{\mathbf{L}}$. The diagonal elements $\rho_{11}$ and $\rho_{22}$ are the probabilities of finding the system in the initial and final potential well. The diffusion motion (now it is the fluctuation of solvent polarization) is slow since it is activated by thermal energy. The off-diagonal terms include not only the diffusion
motion but the high frequency quantum transition behavior $(\gamma(x-\sigma)$ / $h$ term). These properties are important in our future assumptions.

## III. ANALYTICAL EXPRESSION OF RATE CONSTANT

We derived four coupled equations for electron transfer in a polar medium in the last chapter. In this chapter, we are going to derive an approximate expression for the rate constant by using a projection operator method. A consecutive mechanism will be used to separate the diffusive and reactive dynamics (see figure 3). Electron transfer can be expressed as motion from $R A\left(D^{-} A\right.$ ) to $P B$ ( $\mathrm{DA}^{-}$) through an intermediate state I. The boundaries of RA-I and PB-I are located in the region where the tunneling probability is negligible. Such a division has been used in chemical kinetics. An interesting example is given by Northrup and Hynes in ref. 11. A double-well potential surface has been used in a chemical reaction system. The potential surface has been separated into three different regions $R A, P B$ and $I, R A$ and $P B$ correspond to wells and I corresponds to the intermediate region. During the course of the reaction, spatial equilibrium in each well has been obtained. But the intermediate state has been perturbed by passage across the barrier. Thus the intermediate state will deviate from the equilibrium distribution, and this produces a net change of the populations which makes the meaning of the rate constant sensible. Northrup and Hynes use the internal rate constants (which are equal to our $k_{d 1}$ and $k_{d 2}$ ) to describe the rate of approach to equilibrium inside wells RA and PB. The motion within the region of the intermediate state

I is characterized by the barrier rate constants (which are equal to our $k_{n a}^{12}$ and $k_{n a}^{21}$ ) which describe the rate from RA-I to PB-I and vice versa. The final overall rate constants then are geometric sums of the internal rate constant and barrier rate constants. We shall use a similiar point of view in the following discussion.

The kinetic scheme for the occupation probabilities $\mathrm{Na}, \mathrm{Nb}, \mathrm{Ni}$ of the states RA, PB and I is

$$
\begin{array}{ll}
\frac{\partial}{\partial t} N_{i}=-k_{A I} N a+k_{I A} N i & (3.1 a) \\
\frac{\partial}{\partial t} N i=k_{A I} N a-k_{I A} N i-k_{I B} N I+k_{B I} N b & (3 \cdot 1 b) \\
\frac{\partial}{\partial t} N b=k_{I B} N i-k_{B I} N b . & (3.1 c) \tag{3.1b}
\end{array}
$$

To maintain these expressions, the macroscopic quantities $\mathrm{Na}, \mathrm{Nb}$, and Ni should exist; the barrier height should be high enough to obtain an equilibrium state at each potential well and the rate constant should be small enough to be measurable. The macroscopic quantities can exist only when they can be explicitly identified. Distinguishability between Na and Nb exists when RA and PB are well seperated by a high barrier. Passage across the high barrier can perturb the equilibrium distribution in the intermediate state, and make it non-equilibrium. A net change of the populations per unit time in region I produces the reaction rate. In other words, an oscillation of the change of the population from RA to PB which is fast forward and backward can not


Figure 3. Branching ratio diagram for the forward rate constant.
have a reaction rate.
The initial conditions are: $\mathrm{Na}(\mathrm{t}=0)=1, \mathrm{~N}_{1}(\mathrm{t}=0)=0$, and $\mathrm{Nb}(\mathrm{t}=0)=0$.

Using the well-known steady state approximation for the intermediate state $\frac{\partial}{\partial t} N_{1}=0$, we obtain
$\frac{\partial}{\partial t} N a=-\int d \tau \bar{x}_{r}(\tau) N a(t-\tau)+\int d \tau \bar{x}_{r}(\tau) N b(t-\tau)$
$\frac{\partial}{\partial t} N b=\int d \tau \bar{x}_{f}(\tau) N a(t-\tau)-\int d \tau \bar{x}_{r}(\tau) N b(t-\tau)$ ( 3 . 2b )
where the rate kernels $\bar{x}_{f}$ and $\bar{x}_{r}$ are defined as

$$
\begin{align*}
& \bar{x}_{r}=k_{A I} \delta(t)-k_{A I} k_{I A} \exp \left\{-\left(k_{I A}+k_{I B}\right) t\right\} \quad(3.3 a) \\
& \bar{x}_{r}=k_{B I} k_{1 B} \exp \left\{-\left(k_{1 A}+k_{I B}\right) t\right\} . \tag{3.3b}
\end{align*}
$$

Here $\delta(t)$ is the delta function. The memory effect in (eq. (3.2)) means that the rate of change of the stable state population at time $t$ is dependent on the intermediate state population at time $t-\tau$ The intermediate state population depends on the previous gain from and loss to the stable state.

Since we are interested in a long time rate $t>\tau_{i r}$ (trangient time which is the time period required for the maintaining of a
non-equilibrium steady state condition in the intermediate state), the rate expression can be simplified to
$\frac{\partial}{\partial t} \mathrm{Na}=-\mathrm{k}_{12} \mathrm{Na}(\mathrm{t})+\mathrm{k}_{21} \mathrm{Nb}(\mathrm{t})$
( $3.4 a$ )
$\frac{\partial}{\partial t} N b=k_{12} N a(t)-k_{21} N b(t)$
where
$k_{12}=\int d t \bar{x}_{f}(t)$
( $3 \cdot 5 \mathrm{a}$ )
$k_{21}=\int d t \bar{x}_{r}(t)$.

Then the population equations can be written as
$\frac{\partial}{\partial t}\left[\begin{array}{l}\mathrm{Na} \\ \mathrm{Nb}\end{array}\right]=-\left[\begin{array}{lc}k_{12} & -k_{21} \\ -k_{12} & k_{21}\end{array}\right]\left[\begin{array}{l}\mathrm{Na} \\ \mathrm{Nb}\end{array}\right]$

$$
=-\underline{k}\left[\begin{array}{l}
\mathrm{Na}  \tag{3.6}\\
\mathrm{Nb}
\end{array}\right]
$$

and we define
$N a=\int_{-\infty}^{\infty} d x \rho_{11}(x, t)$
$N b=\int_{-\infty}^{\infty} d x \rho_{22}(x, t)$
in our case.
After Laplace transformation, $\hat{f}(s)=\int_{0}^{\infty} e^{-s t} F(t) d t$, we have

$$
\begin{equation*}
[s \mathbf{I}+\underline{k}] \hat{N}(s)=\underline{N}(t=0) \tag{3.7}
\end{equation*}
$$

The reason to do this Laplace transformation is: There are an infinite number of relaxation modes which are distributed from low to high frequency. The slow ET rate is assumed to have a comparable rate to the slowest relaxation frequency (of course not in the low barrier and activationless regimes). If a long time rate exists, we want to extract this slowest process from the fast relaxation modes. Letting s $\rightarrow 0$ (i.e. $t \rightarrow \infty$ ), we can get a long-time rate expression. Fortunately, our four coupled equations of eq. (2.36) can be reduced to two coupled equations similar to the reduction to eq. (3.16) and the rate expression can be identified by using a projection operator method. We now carry out this reduction. The formal solution of eq. (2.36c) is

$$
\begin{gather*}
\rho_{12}=-\frac{V_{12}}{\hbar} \int d x_{i} \int d t_{i} G_{12}\left(x, t \mid x_{i}, t_{i}\right) \\
 \tag{3.8}\\
{\left[\rho_{22}\left(x_{i}, t_{i}\right)-\rho_{11}\left(x_{i}, t_{i}\right)\right]}
\end{gather*}
$$

where

$$
\begin{aligned}
G_{12}= & {\left[\frac{\partial}{\partial t}-L_{12}+i\left(v_{11}-v_{22}\right) / \hbar\right]^{-1} } \\
= & \frac{1}{2 \sqrt{2 \pi}} \frac{1}{\sqrt{D \tau_{L}(1-\exp (-2 t))}} \exp \left\{\frac{1}{2}\right. \\
& \frac{1}{D \tau_{L}(1-\exp (-2 t))}\left[2 D \frac{\gamma \tau_{L}^{2}}{\hbar}\left(1-e^{-t}\right)\right.
\end{aligned}
$$

$$
\begin{aligned}
& \left.-i\left[x-x_{i} e^{-t}-\frac{1}{2} x_{0}\left(1-e^{-t}\right)\right]\right]^{2}-D\left(\frac{\gamma \tau_{L}}{h}\right)^{2} \tau_{L} t \\
& \left.+i \frac{\gamma r_{L}}{h}\left(x-x_{i}-\frac{1}{2} x_{0} t+\sigma t\right)\right\} \\
& L_{12}=D \frac{\partial}{\partial x}\left[\frac{\partial}{\partial x}+\beta \frac{\partial}{\partial x}\left(\frac{V_{11}+V_{22}}{2}\right)\right] \\
& \text { for the potential of eq. (4.1). }
\end{aligned}
$$

This propagator includes both the motion induced by the stochastic process, $L_{12}$, and the surface splitting, $\left(V_{22}-V_{11}\right)$, for the tunneling effect. As we discussed in the last chapter, the diffusion along the reaction coordinate is treated classically because its characteristic frequency $\omega \simeq 1 \mathrm{~cm}^{-1}$ (i.e. smaller than $k_{B} T / h$ ) is lower than the quantum transition frequency $\omega \simeq 1000 \mathrm{~cm}^{-1}$ (i.e. $y(x-$ $\sigma$ ) /h). Assuming the time variation of $\mathbf{G}_{12}$ is faster than that of the local population difference, $\left[\rho_{22}(x, t)-\rho_{11}(x, t)\right]$, then

$$
\rho_{12}=-i \int d x_{i} \bar{K}_{12}\left(x \mid x_{i}\right)\left[\rho_{22}\left(x_{i}, t\right)-\rho_{11}\left(x_{i}, t\right)\right]
$$

here
$\bar{K}_{12}\left(x \mid x_{i}\right)=\frac{V_{12}}{\hbar} \int d \tau G_{12}\left(x, \tau \mid x_{i}, 0\right)$
(in $G_{12}$, the $\frac{i \gamma \tau_{L}}{h}\left(\sigma-\frac{1}{2} x_{0}\right) t$ term shows that the oscillation frequency will increase as $t$ increases).

The formal solution of eq. (2.36a) with eq. (3.10) yields
$\rho_{11}(x, t)=\frac{V}{h} \int d x_{1} \int d x_{1} \int d \tau G_{11}\left(x, \tau \mid x_{1}, 0\right)$

$$
\bar{K}_{12}\left(x_{1} \mid x_{1}\right)\left[\rho_{22}\left(x_{1}, t\right)-\rho_{11}\left(x_{1}, t\right)\right],
$$

where $G_{11}$ is the propagator corresponding to $\left[\frac{\partial}{\partial t}-L_{11}\right]^{-1} \cdot G_{11}$ describes the motion in well A. If we assume its spatial variation (with frequency smaller than $k_{B} T / h$ ) is slow relative to that of $\bar{K}_{12}($ with frequency $\gamma(x-\sigma) / \hbar)\left(\right.$ see $i \frac{\gamma \tau_{L}}{\hbar} x$ term in $\bar{K}_{12}$ ), then
$\rho_{11}=\frac{V_{12}}{\hbar} \int d x_{1} \int_{0}^{\infty} d \tau G_{11}\left(x, \tau \mid x_{1}\right)\left[\int d x_{i} \bar{K}_{12}\left(x_{1} \mid x_{i}\right)\right.$

$$
\begin{equation*}
\left.\cdot\left[\rho_{22}\left(x_{i}, t\right)-\rho_{11}\left(x_{i}, t\right)\right]\right] \tag{3.13}
\end{equation*}
$$

This is the key assumption and leads ultimately to the consecutive rate scheme. Note that we separated the diffusion ( $G_{11}$ ) motion and the transition ( $\bar{K}_{12}$ ) behavior in this equation. That is the basis of a consecutive mechanism.

We define
$K_{12}\left(x ; x^{*}\right)=-\frac{V_{12}}{h} \int d x_{1} \bar{K}_{12}\left(x_{1} \mid x\right)$

$$
=\left(\frac{v_{12}}{h}\right)^{2} \int d x_{1} \int_{0}^{\infty} d \tau G_{12}\left(x_{1}, \tau \mid x, 0\right)
$$

Applying $G_{11}^{-1}$ to eq. (3.13), we obtain

$$
\left[\frac{\partial}{\partial t}-L_{11}\right] \rho_{11}=2 \operatorname{Re} K_{12}\left(x ; x^{*}\right)
$$

$$
\begin{equation*}
\left[\rho_{22}(x, t)-\rho_{11}(x, t)\right] \tag{3.15}
\end{equation*}
$$

A similiar treatment of $\rho_{22}$ gives us the final two coupled equations

$$
\begin{equation*}
\frac{\partial}{\partial \underline{t}} \underline{\rho}=[\underline{\underline{L}}+\underline{k}] \underline{\rho} \tag{3.16}
\end{equation*}
$$

with
$\underline{\rho}=\left[\begin{array}{l}\rho_{11} \\ \rho_{22}\end{array}\right]$
$\underline{L}=\left[\begin{array}{ll}L_{11} & 0 \\ 0 & L_{22}\end{array}\right]$
$\underline{\underline{K}}=2 \operatorname{ReK} K_{12}\left[\begin{array}{lr}1 & -1 \\ -1 & 1\end{array}\right] ;$
the $K$ term can also be thought of as a sink term as discussed in ref. 18.

The projection operator method will now be used to separate the diffusive and reactive dynamics. The reactive dynamics arise from the equilibrium part of the rate kernels, see eq. (3.16).

We define the projection operator $P=\int d x$ and its complement $\underline{\underline{Q}}$ $=1$ - $\underline{\underline{p}}$, where
$\underline{g}=\left[\begin{array}{ll}g_{1} & 0 \\ 0 & g_{2}\end{array}\right], \quad g_{i}=\exp \left(-\beta V_{i i}\right) / \int_{-\infty}^{\infty} d x \exp \left(-\beta V_{i 1}\right)$.

By applying $\underset{=}{P}$ and $Q$ to Laplace transformation of eq. (3.16), we get
$\left\{s \underline{1}+\left[\underline{\underline{P}} \underline{\underline{K}}-[8 \underline{\underline{Q}}(\underline{\underline{L}}+\underline{\underline{k}})]^{-1} \underline{\underline{Q}}(\underline{\underline{L}}+\underline{\underline{K}})\right]\right\} \underline{\underline{p}} \underline{\underline{\rho}}(\mathrm{~s})$
$=\underline{\mathrm{P}} \underline{\rho}(\mathrm{t}=0)$.

In obtaining this expression, we have used $\underline{\underline{E}} \underline{\underline{L}}=0$ (this projects out the diffusive motion), the boundary condition $\underline{\rho} \rightarrow 0$ as $x \rightarrow \pm \propto$ and $\underline{\underline{E}}=0$ for the equilibrium distribution conditions in each well. Comparing with the reaction kernel in eq. (3.7), we can identify the rate kernel as

$$
\underline{\underline{K}}=\lim _{\underline{0} \rightarrow} \underline{g}^{-1}\left\{\underline{\underline{E}} \underline{\underline{E}} \underline{\underline{E}}\left[\mathrm{~B}+\underline{\underline{Q}}(\underline{\underline{L}}+\underline{\underline{K}})^{-1} \underline{Q}(\underline{Q}+\underline{K})\right]\right\} \underline{\underline{G}}
$$

The first term describes the instantaneous rate constant which is obtained by assuming equilibrium in the donor and acceptor wells. The second term accounts for the non-equilibrium effects caused by diffusion and reaction dynamics.

After simplification of the formal expression (see Appendix A),
we get
$k_{12}=\frac{\cdot}{1+k_{n a}^{12} / k_{d 1}^{12}+k_{n a}^{21} / k_{d 2}}$
and

$$
\begin{equation*}
k_{21}=\frac{k_{n a}^{21}}{1+k_{n a}^{12} / k_{d 1}+k_{n a}^{21} / k_{d 2}}, \tag{3.19b}
\end{equation*}
$$

where
$k_{d i}^{-1}=\int_{0}^{\infty} d t\left[G_{1 i}^{0}\left(x ; x^{*}, t\right) g_{i}^{-1}\left(x^{*}\right)-1\right]$
and

$$
k_{n a}^{i j}=\int d x K_{i j}\left(x ; x^{*}\right) g_{i}(x)
$$

The $k_{d i}$ are the internal rate constants which describe the approach to equilibrium in each well. The non-adiabatic transition rate $k_{n a}^{i j}$ is a surface crossing rate which depends on the initial equilibrium distribution $g_{i}$ and the transition term in the intermediate region. Our $K_{i j}$ is derived from $G_{12}$ (see eq. (3.14)). For large friction it is convenient to use $G_{11}$ (see ref. 10), because the difference between $G_{11}$ and $G_{12}$ is small. For moderate friction, their difference must be treated explicitly.

The formula that we get for the rate constant can be explained by using a branching diagram (see figure 3). In this diagram, $k$ d represents the diffusion rate in surface $R A$, starting from an equilibrium distribution. $P_{f}=k_{n a}^{12} /\left(k_{d 1}+k_{n a}^{12}\right)$ is the probability
of reaching the PB-I boundary rather than staying at RA. $P_{b}=k_{d 2} /$ ( $k_{d 2}+k_{n a}^{21}$ ) is the probability of staying at $P B$ rather than crossing back to RA-I. The total foward rate constant should include the one way flux and all of the recrossing trajectories, so

$$
\begin{align*}
& k_{12}=k_{d 1} P_{f}\left\{\sum_{j=0}^{\infty}\left[\left(1-P_{b}\right) P_{f}\right]^{j}\right\} P_{b} \\
& =k_{d 1} P_{f} P_{b} /\left[1-P_{f}\left(1-P_{b}\right)\right] \\
& =\frac{\frac{k_{n a}^{12}}{\left(k_{d 1}+k_{n a}^{12}\right)} \cdot \frac{k_{d 2}}{\left(k_{d 2}+k_{n a}^{12}\right)}}{\frac{k_{n a}^{12}}{\left(k_{d 1}+k_{n a}^{12}\right)} \frac{k_{n a}^{21}}{\left(k_{d 2}+k_{n a}^{21}\right)}} \\
& =\frac{k_{n a}^{12}}{1+k_{n a}^{12} / k_{d 1}+k_{n a}^{21} / k_{d 2}}, \tag{3.20}
\end{align*}
$$

and similiarly for $k_{21}$.

If the passage to $P B$ is irreversible (i.e. $k_{n a}^{21}=0$ ), then $k_{12}=k_{n a}^{12} /\left(1+k_{n a}^{12} / k_{d 1}\right)$.

This is the one way reaction rate. The ratio $k_{12} / k_{21}=k_{n a}^{12} / k_{n a}^{21}=$ $K_{n a}^{e q}$, and satisfies detailed balance.

If $k_{n a}^{12}<k_{d 1}$, the rate determining step will be the non-adiabatic transition rate $k_{n a}^{12}$. If $k_{n a}^{12}>k_{d 1}$, the rate determining
step will be the diffusion rate $k_{d 1^{\circ}}$ Thus, the solvent controlled transition from a non-adiabatic to adiabatic rate constant is involved in our rate expression. Sometimes conditions can satisfy $k_{n a}^{12} / k_{d i} \ll 1$, $k_{n a}^{21} / k_{d 2} \gg 1$, i.e. the system reaches an equilibrium state in RA very fast and is slowly stabilized in PB. The forward rate then is $k_{12}=k_{\text {na }}^{12}$ $k_{d 2} / k_{n a}^{21}$ and the rate is controlled by the rate of stabilization in PB. The equilibrium constant $K_{n a}^{e q}=k_{n a}^{12} / k_{n a}^{21}$, so the forward rate is independent of ET rate. This can happen for an endothermic reaction.

The $k_{d i}$ rate constants describe the rate of approaching equilibrium in each well in the absence of the reaction. The propagator $G_{i i}\left(x^{*}, t \mid x^{*}, 0\right)$ describes the probability density for being at the crossing point $x^{*}$ at time $t$, given that the particle is at $x^{*}$ at time $t=0$. The average time for the particle's evolution until it reaches equilibrium, starting from $x^{*}$, is $k_{d i}^{-1}$. For barrier heights $\beta$ Ea $>5$, we can use the Arrhenius reaction rate $\left(k_{d}^{A r r}=\frac{1}{\tau_{L}}\left(\frac{\beta \text { Ea }}{\pi}\right)^{1 / 2} \exp (-\beta \operatorname{Ea})\right)$ instead of using $k_{d i}^{-1}=g_{i}^{-1} \int\left(G_{i i}-g_{i}\right) d t$ (see figure 4). As we can see, for $\beta \mathrm{Ea}>5$, they match very well.

The rate constant $k_{n \varepsilon}^{12}$ describes, through $G_{12}$ the stochastic process and surface crossing transition in the neighbourhood of the crossing point starting from the equilibrium initial well RA (see eq. (3.19d)). This off-diagonal propagator $G_{12}$ describes the transition process (see Appendix B) as

$$
K_{12}\left(x ; x^{*}\right)=\left(\frac{a}{4}\right)^{2} \frac{1}{\lambda} \operatorname{Re} \int d t \exp \left\{-i x \frac{\gamma \tau_{L}}{\hbar}\left(1-e^{-t}\right)\right.
$$

$$
\begin{align*}
& +i \frac{\gamma \tau_{L}}{h}\left[\frac{1}{2} x_{0}\left(1-t-e^{-t}\right)+t \sigma\right] \\
& \left.-A \lambda^{2}\left[-3+2 t+4 e^{-t}-e^{-2 t}\right]\right\} \tag{3.22}
\end{align*}
$$

where $\gamma=k_{w} x_{0}=\Delta F$ and $\Delta F$ is the difference of slope (or force) at the crossing point.

In the normal region, $x_{0} \rightarrow$ large (i.e. the separation of the wells is large, see figure 1 c ), this implies $1_{\mathrm{TS}}, 1_{\mathrm{LZ}} \rightarrow 0$, and we get more localized behavior. In the inverted region, $x_{0} \rightarrow 0$, then $I_{\text {TS }} \mathbf{I}_{\text {LZ }}$ $\rightarrow$ large, and the quantum behavior becomes more obvious. The interesting region that we discussed in the Introduction is $\lambda \geqslant 1$, (overdamped region), and inverted region ( $A$ is small). If we assume $A \lambda^{2}>1$, then only the short time behavior in eq. (3.22) is important. Then
$K_{12}\left(x ; x^{*}\right)=\left(\frac{a}{4}\right) \frac{1}{\lambda} \operatorname{Re} \int d t \exp \left\{-i \frac{\gamma r_{L}}{h}[(x-\sigma) t\right.$

$$
\begin{align*}
& \left.+\frac{1}{2}\left(\frac{1}{2} x_{0}-x\right) t^{2}\right]-\left[\frac{2}{3} A \lambda^{2}+\frac{1}{6} x \frac{-i \gamma \tau_{L}}{h}\right. \\
& \left.\left.-\frac{1}{12} x_{0} \frac{-i \gamma \tau_{L}}{h}\right]\right\} . \tag{3.23}
\end{align*}
$$

To accurately describe the delocalization width, $\mu$, is very difficult. We define it qualitatively as the ratio of the $1 / 3$ power of the coefficient of $t^{3}$ and $t$, and we have
$\mu=|x-\sigma|$


Figure 4. Plot of $1 /\left(k_{d} \tau_{L}\right)$ versus $\beta \in E_{m}\left(\longrightarrow\right.$ corresponds to $k_{d i}(\cdot)$ corresponds to $k_{d}^{A r r}$.

$$
\begin{align*}
& =\frac{\gamma \tau_{L}}{\hbar} /\left[\frac{2}{3} A \lambda^{2}\right]^{1 / 3} \\
& \simeq\left(x_{0} \tau_{L}\right)^{-1 / 3} . \tag{3.24}
\end{align*}
$$

As the friction increases (i.e. $\tau_{L} \rightarrow$ large), the delocalization width $\mu$ will shrink to 0 (i.e. localized transition). The small $x_{0}$ (inverted region) will increase $\mu$. After the integration over $x$ in $k_{n a}^{12}$ (see eq. (3.19d)), we have

$$
\begin{align*}
k_{n a}^{12}= & \left(\frac{a}{4}\right)^{2} \frac{1}{\lambda} \int_{0}^{\infty} d t \cos \left[\lambda\left(S\left(1-e^{-t}\right)-P t\right]\right. \\
& \exp \left\{-A \lambda^{2}\left[e^{-t}-1+t\right]\right\} . \tag{3.25}
\end{align*}
$$

When $A \lambda^{2} \gg 1$, the short time expansion is appropriate, and we obtain

$$
\begin{align*}
k_{n a}^{12} & =\left(\frac{a}{4}\right)^{2} \frac{1}{\lambda} \int d t \cos [\lambda B t] \exp \left\{-\frac{A \lambda^{2}}{2} t\right\} \\
& =\frac{1}{2} \sqrt{\frac{2 \pi}{A \lambda^{2}}} \exp \left\{-\frac{B}{2}^{2}\right\} \tag{3.26}
\end{align*}
$$

As we can see, in the last equation there are no friction effects in the exponential term. This means that in the extreme overdamped regime, the transition rate depends on the barrier height only. The width of splitting is zero (relative to the diffusion length), and it is a localized transition. This localized transition gives us the Arrhenius


Figure 5. Plot of $k_{n=}^{12} \times 10^{-3}$ versus $\lambda$. $(\times)$ for $G_{12}$ in eq. (3.19d), (-) for $G_{11}$ in eq. (3.19d). $A=0.06, S=0.05, P=-4$., $h \omega=300 \mathrm{~cm}^{-1}, \mathrm{~V}_{12}=0.3 \mathrm{~cm}^{-1}, \mathrm{~T}=300 \mathrm{~K}$.
result.

When $A \lambda^{2}$ is not too large, $\lambda$ should influence the activation part (i.e. exponential part). As we can see from figure 4, ( $x$ means $k_{n a}^{12}$ is calculated with the use of $G_{12}$ and $o$ is calculated with the use of $G_{11}$ ), which is in the inverted region, our $k_{n a}^{12}$ will decrease as the friction increases. If we increase the friction to have large $A \lambda^{2}$, then $k_{n a}^{12}$ will approach $k_{n a}^{A r r}$ which is independent of friction. Also we can see that the difference between $k_{n a}^{12}\left(f r o m G_{12}\right)$ and $k_{n a}^{12}$ (from $G_{11}$ ) is large when $\lambda$ (friction) is moderate.

To conclude this chapter, the key step in getting the consecutive rate expression is the assumption that the spatial variation of $\mathbf{G}_{11}$ is slower than that of $\overline{\mathrm{K}}_{12^{\circ}}$ This separates the diffusion and transition parts of eq. (3.10). So we have two different rates in the wells and the intermediate region. The behavior of the transition depends on the relative size of the splitting width $\mu$ and diffusion length $1_{f}$ If the diffusion length is smaller than $\mu$, then within the length $\mu$ the system is still undergoing diffusion motion and the friction effect is obvious. If the diffusion length is larger than $\mu$ then within the transition region the system will not feel the friction effects. Therefore, the quantum behavior of the transition can be reduced to a classical (i.e. localized) transition by increasing the friction. Friction effects (i.e. solvent dynamic effects) will contribute to our $k_{n a}^{i j}$. The solvent controlled transition fron non-adiabatic to adiabatic behavior is obtained in our result.

## IV. NUMERICAL SOLUTION OF COUPLED EQUATIONS

We have solved the reduced Zusman equations eq. (3.10) by using a projection operator method and obtained approximate analytic expressions for the rate constants. The consecutive mechanism relies on the separation of diffusive and reactive dynamics. To go beyond the region of $1>\mu$, when the transition is no longer confined to the crossing point, a unified method should be used. In this chapter we solve the Zusman equations exactly for the long-time reaction rate. The Fokker-Planck operator describing the Brownian motion in the harmonic potential surfaces can be cast into a tri-diagonal vector recurrence relation by basis expansion of the probability density. The Zusman equations with four coupled (second order in space, first order in time) differential equations can be transformed into four coupled first order (in time) differential equations. A vector form of first order differential equations is obtained. The Laplace transformation of its solution can change this first order vector differential equation into an eigen-value problem. We can identify the reversible forward and backward reaction rates with the smallest non-zero eigen-value. The efficient way to solve for this small eigen-value is to use tri-diagonal vector recurrence relations, from which a matrix continued fraction equation is obtained. This method has the advantage that without the detailed balance condition we still can get accurate and fast results. For computer programming, it is a good method especially
to save space.

We use the harmonic potential surfaces
$v_{11}=\frac{1}{2} k_{w} x^{2}$
$v_{22}=\frac{1}{2} k_{v}\left(x-x_{0}\right)+v_{0}$.
(4.1)

The stochastic processes corresponding to overdamped Brownian motion are
$L_{i i}=D \frac{\partial}{\partial \pi}\left[\frac{\partial}{\partial x}+\beta \frac{\partial}{\partial x} v_{i i}\right], i=1,2$
also
$L_{12}=L_{21}=\frac{1}{2}\left(L_{11}+L_{22}\right)$.

To simplify the calculation, we need to rearrange the definition of the density matrix and have the same differential operator for its elements. Also we can eliminate the complex components. This can simplify the computer calculation.

We define our new density matrix elements as
$\rho^{ \pm}=\left(\rho_{11} \pm \rho_{22}\right)$
$2 \operatorname{Re} \rho_{12}=\rho_{12}+\rho_{21}$
$2 \operatorname{Im} \rho_{12}=\rho_{12}-\rho_{21}$
(4.4c)

With these definitions, the Zusman equations can be written as

Now we introduce a basis set expansion of our new density matrix:

$$
\begin{align*}
& \rho^{ \pm}=\sum_{n=0}^{\infty} a_{n}^{ \pm}(t) r_{n}(y / \sqrt{2}) \\
& \operatorname{Re} \rho_{12}=\sum_{n=0}^{\infty} b_{n}^{+}(t) r_{n}(y / \sqrt{2}) \tag{4.6b}
\end{align*}
$$

$$
\operatorname{Im} \rho_{12}=\sum_{n=0}^{\infty} b_{n}^{-}(t) r_{n}(y / \sqrt{2}) .
$$

The argument $y=x-\frac{1}{2} x_{0}$. The set $\left\{r_{n}\right\}$ are the right eigen-functions of the Fokker-Planck operator $L_{12}$ :

$$
\begin{equation*}
\left[\frac{\partial^{2}}{\partial x^{2}}+\left(x-\frac{1}{2} x_{0}\right) \frac{\partial}{\partial x}+1\right] r_{n}=\mu_{n} r_{n} \tag{4.7}
\end{equation*}
$$

$$
\begin{align*}
& \frac{\partial}{\partial t} \rho^{+}=\left[\frac{\partial^{2}}{\partial x^{2}}+\left(x-\frac{1}{2} x_{0}\right) \frac{\partial}{\partial x}+1\right] \rho^{+}+\frac{1}{2} x_{0} \frac{\partial}{\partial x} \rho^{-}(4.5 a) \\
& \frac{\partial}{\partial x} \rho^{-}=\left[\frac{\partial^{2}}{\partial x^{2}}+\left(x-\frac{1}{2} x_{0}\right) \frac{\partial}{\partial x}+1\right] \rho^{-}+\frac{1}{2} x_{0} \frac{\partial}{\partial x} \rho^{+}-a \operatorname{Im} \rho_{12} \\
& \text { (4.5b) } \\
& \frac{\partial}{\partial t} \operatorname{Re} \rho_{12}=\left[\frac{\partial^{2}}{\partial x^{2}}+\left(x-\frac{1}{2} x_{0}\right) \frac{\partial}{\partial x}+1\right] \operatorname{Re} \rho_{12} \\
& +b(x-\sigma) \operatorname{Im} \rho_{12} \\
& \frac{\partial}{\partial t} \operatorname{Im} \rho_{12}=\left[\frac{\partial^{2}}{\partial x^{2}}+\left(x-\frac{1}{2} x_{0}\right) \frac{\partial}{\partial x}+1\right] \operatorname{Im} \rho_{12} \\
& -b(x-\sigma) \operatorname{Re} \rho_{12}+\frac{a}{4} \rho^{-} .
\end{align*}
$$

with
$r_{n}=\left(2^{n} n!\right)^{-1 / 2}\left(\frac{1}{2 \pi}\right)^{1 / 4} e^{-\frac{1}{2} y^{2}} H_{n}\left(\frac{1}{\sqrt{2}} y\right)$
and
$\mu_{n}=-n, n=0,1,2, \ldots$
(see Appendix C for details).

The left-hand eigen-function $\left\{\left\{_{n}\right.\right.$ \} also has been introduced and the integration over $x$ leads to

$$
\begin{aligned}
& \frac{\partial}{\partial t} a_{n}^{+}=\mu_{n} a_{n}^{+}-\frac{1}{2} x_{0} \sqrt{n} a_{n-1}^{-} \\
& \frac{\partial}{\partial t} a_{n}^{-}=\mu_{n} a_{n}^{-}-\frac{1}{2} x_{0} \sqrt{n} a_{n-1}^{-}-a b_{n}^{-} \\
& \frac{\partial}{\partial t} b_{n}^{+}=\mu_{n} b_{n}^{+}+b \sqrt{n} b_{n-1}^{-}+b \sqrt{n+1} b_{n+1}^{-}-b \sigma_{y} b_{n}^{-} \quad(4.8 b) \\
& \frac{\partial}{\partial t} b_{n}^{-}=\mu_{n} b_{n}^{-}-b \sqrt{n} b_{n-1}^{+}-b \sqrt{n+1} b_{n+1}^{+}+b \sigma_{y} b_{n}^{+}+\frac{1}{4} a a_{n}^{-} \\
& \text {(4.8d) }
\end{aligned}
$$

We assemble all of the coefficients into a matrix form
$\bar{d} \frac{\mathbf{d}}{\mathbf{t}} \underline{v}(\mathrm{t})=\underline{M} \underline{\mathrm{~V}}(\mathrm{t})$
where
$\underline{v}(t)=\left[a_{0}^{+}, a_{0}^{-}, b_{0}^{+}, b_{0}^{-} ; a_{1}^{+}, a_{1}^{-}, b_{1}^{+}, b_{1}^{-} ; \ldots\right]^{T}$
is a column vector of the time-dependent coefficients.

## Rate expression:

The formal solution of eq. (4.9) is
$\underline{v}(t)=e^{\underline{\underline{L}} t} \underline{v}(0)$.

This formal expression can be rewritten in terms of the eigen-functions and eigen-values of $\underline{M}$.

Let
$\underline{L}_{j}^{\prime} \underline{M}=\Lambda_{j}^{\prime} \underline{L}_{j}^{\prime}$
 ( $4 \cdot 11 b$ )
non-degeneracy implies $\underline{L}$, and $\underline{R}$, are orthogonal, i.e.
$\underline{L}_{j}^{\prime} \underline{R}_{k}=\delta_{j k}$


Thus,

$$
\begin{align*}
\underline{v}(t) & =\sum_{j=0}^{\infty}\left[\underline{L}_{j}^{\prime} \underline{v}(0)\right] \underline{R}_{j} e^{\Lambda_{j} t} \\
& =c_{0} \underline{R}_{0}+\sum_{j=1}^{\infty} c_{j} \underline{R}_{j} e^{\Lambda_{j} t}, \tag{4.13}
\end{align*}
$$

where
$c_{j}=\underline{L}_{j}^{j} \underline{v}(0)$

This shows a multi-exponential relaxation process or modes of fluctuation in the solvent. The eigen-values are the relaxation frequencies. We can show, from the conservation of probability, that $\Lambda_{0}$ $=0$ and $c_{0} R_{0,0}=1$.

Recalling the rate expression from Chapter III, our scheme is
$\mathrm{A} \rightleftarrows \mathrm{B}$
$\frac{d}{d}\left[\begin{array}{l}\mathrm{Na} \\ \mathrm{Nb}\end{array}\right]=\left[\begin{array}{rr}-k_{12} & k_{21} \\ \mathbf{k}_{12} & -k_{21}\end{array}\right]\left[\begin{array}{l}\mathrm{Na} \\ \mathrm{Nb}\end{array}\right]$
$\mathrm{Na}+\mathrm{Nb}=1$
$k_{12}+k_{21}=\tau_{.}$

The exact solution of this equation is
$N a(t)=e^{-t \tau}\left[\int_{0}^{t} k_{21} e^{\tau x} d x+N(0)\right], N(0)=1$

$$
\begin{equation*}
=\frac{k_{21}}{\tau}+\frac{k_{12}}{\tau} e^{-\tau \tau} . \tag{4.14}
\end{equation*}
$$

Now from the definition
$N a(t)=\int_{-\infty}^{\infty} \rho_{11}(x, t) d x$

$$
\begin{align*}
& =\frac{1}{2} \int_{-\infty}^{\infty}\left[\rho^{+}+\rho^{-}\right] d x \\
& =\frac{1}{2} \sum_{n=0}^{\infty}\left[a_{n}^{+}(t)+a_{n}^{-}(t)\right] \int_{-\infty}^{\infty} r_{n}\left(x-\frac{1}{2} x_{0}\right) d x \\
& =\frac{1}{2} \sum_{n=0}^{\infty}\left[a_{n}^{+}(t)+a_{n}^{-}(t)\right] \int_{-\infty}^{\infty} r_{n}(x) d x \\
& =\frac{1}{2}(2 \pi)^{1 / 4}\left(a_{0}^{+}(t)+a_{0}^{-}(t)\right) . \tag{4.15}
\end{align*}
$$

Also from probability conservation

$$
\begin{align*}
& \int_{-\infty}^{\infty}\left(\rho_{11}(x, t)+\rho_{22}(x, t)\right) d x \\
& =\int_{-\infty}^{\infty} \rho^{+}(x, t) d x \\
& =\int_{-\infty}^{\infty}\left[\sum_{n=0}^{\infty} a_{n}^{+}(t) r_{n}\left(x-\frac{1}{2} x_{0}\right)\right] d x \\
& =\sum_{n=0}^{\infty} a_{n}^{+}(t) \int_{-\infty}^{\infty} r_{n}(y) d y, y=x-\frac{1}{2} x_{0} \\
& =(2 \pi)^{1 / 4} a_{0}^{+}(t) \\
& =1 . \tag{4.16}
\end{align*}
$$

## So we have

$N:(t)=\frac{k_{21}}{\tau}+\frac{k_{12}}{\tau} e^{-\tau t}$

$$
\begin{equation*}
=\frac{1}{2}\left[1+(2 \pi)^{1 / 4} a_{0}^{-}(t)\right] \tag{4.17}
\end{equation*}
$$

i.e.
$(2 \pi)^{1 / 4} a_{0}^{-}(t)=\left(\frac{2 k_{21}}{\tau}-1\right)+\frac{2 k_{12}}{\tau} e^{-\tau t}$.

Comparing eq. (4.13) and eq. (4.18)
$k_{21}=-\left(\frac{R_{1,0}}{R_{0,0}}+1\right) \Lambda_{1} / 2$
$k_{12}=-\Lambda_{1}-k_{21}$.

The quantities that we are going to calculate now are $\Lambda_{1}$ and $R_{1,0} / R_{0,0}$ of the matrices $\underline{M}$. The method of solution relies on the useful feature that $\underline{\underline{M}}$ is a block tri-diagonal matrix, where the blocks are $4 \times 4$ matrices, corresponding to the four coefficients $a_{i}^{ \pm}, b_{i}^{ \pm}$for $a$ given i. This tri-diagonal matrix actually satisfies a vector recurrence relationship. The details of the method are presented in Appendix D.

From the structure of the zeroth $4 \times 4$ block, there is at least one zero eigen-value corresponding to the equilibrium state. Of the three other eigen-values, one is real and corresponds to $1 /\left(k_{12}+\right.$ $k_{21}$ ), and the other two are complex conjugates. For the existence of the reaction rate, $\Lambda_{1}<\Lambda_{2}-\Lambda_{1}$ (where $0=\Lambda_{0}<\Lambda_{1}<\Lambda_{2}<\ldots$ ) and $R_{1,0}<R_{1,1}$ must be satisfied. Otherwise, an initial condition dependent rate constant expression should include all of the relaxation modes. It will be observed in the ativationless region.

## V. RESULTS AND DISCUSSION

The numerical results of our algorithm can be checked with the crossing rate of Arrhenius' result (i.e. $k_{n a}^{A r r}=\left(V_{12}^{2} / 2 h\right)$ $\left.\left(\frac{\pi}{\beta E a}\right)^{1 / 2} e^{-\beta E a}\right)$ at high barrier. Table 1 shows Ea $=B^{2} / 2 A=2.69$ and the friction changes from $\lambda=10$ to 500 . As we can see when we increase the friction, the ratio $k_{12} / k_{n a}^{T S T}<k_{12} / k_{12}^{i r r}<k_{12} / \mathbf{k}_{12}^{\text {rev }}$, but all of the ratio are close to one. This means, for the normal region, with small splitting of the delocalization width, we can get the Arrhenius result from our numerical method.

To check the validity of the consecutive mechanism, the parameters were chosen to have approximately equal diffusive ( $k_{d 1}$, $\left.k_{d 2}\right)$ and crossing $\left(k_{n a}^{12}, k_{n a}^{21}\right)$ contributions in the approximate rate expression eq. (3.19a,b). In this situation, the effect of non-separability of the dynamics will be explicit (i.e. the assumption of eq. (3.10) will not be valid).

The friction values ranging from $\tau_{L}=10 / 3$ to $200 / 3$ represent liquids with moderate to large $\tau_{L}$ values. The range $\tau_{l}=1000 / 3$ to 2000/3 may represent a protein solvent. The electronic matrix element $V_{12}$ is chosen to satisfy $t_{d}=\left(V_{12}^{2} / h\right)\left[\left|d\left(V_{11}-V_{22}\right) / d x\right| D^{1 / 2}\right.$ $]^{-1 / 3}$ for non-adiabatic transitions (see ref. 9). This is the condition for the validity of perturbation theory. If this condition is violated,
for example, for large friction, the transition which is non-adiabatic in the ballistic region will change into an adiabatic transition.

The factors in eq. (3.19 a,b) must be evaluated. The diffusion rates $k_{d 1}$ and $k_{d 2}$ are obtained by direct integration of eq. (3.19c). The non-adiabatic rate constants $k_{n a}^{12}$ and $k_{n a}^{21}$ are defined in eq. (3.19d) They would follow directly from a Golden-rule calculation, with the propagator corresponding to evolution on the averaged surface.

The results presented in Table 2 show that for sufficiently inverted behavior the overall rate cannot be broken up into the consecutive steps of diffusion in the donor well and surface crossing. The width of the surface crossing region becomes so large, due to nuclear tunneling, that this separation can no longer be made.

For not too inverted behavior, Table 2 shows that the approximate expression is good, when $k_{n a}^{1 j}$ is evaluated by incorporating the nuclear tunneling effect. That is, if we were to use $k_{n a}^{\text {TST }}$ instead of $k_{n a}^{i j}$, the result would be completely incorrect.

For future work, we can expand our present work to include activationless ET with a localized initial condition (a delta function) which is different from our gaussian equilibrium distribution. In the activationless case, there is no barrier, and the reaction rate is very fast. Before the equilibrium is reached, the reaction may be finished. Therefore, we should consider all of the following factors: 1) a delta function initial distribution. 2) For the activationless case, the
reaction rate is governed by the shorter time dynamics rather than by the longer time dynamics. Thus the high frequency relaxation modes (i.e. high frequency friction) are most important. Rips and Jortner use Zusman's method to find the activationless solvent-controlled ET rate with thermal equilibrium and a localized initial state. Qualitatively, they found when the initial state is in thermal equilibrium, within a relevant time $t / \tau_{L}<4$, an asymptotic rate expression is in good agreement with activationless ET kinetics. In the localized initial state, the system will move from its initial position to the bottom of the initial well. The time it takes is called the delay time $t^{*}$ which is smaller than the thermalization time. For $t>t^{*}$, a single exponential decay description is appropriate. Our numerical algorithm gives a quantitative understanding of the contribution of the fast relaxation modes to the transition rate (i.e. the modes in eq. (4.13) with $j \geq 2$ should be considered, because the splitting of the eigen-values between $\Lambda_{1}$ and $\Lambda_{2}$ is small).

In the two crossing point case, Kakitani and Mataga et. al. ${ }^{19}$ have argued that the force constant of the potential well should increase significantly when the solute charge is increased (for example, the reaction $A^{+} B^{-} \rightarrow A B$ ) and the $E T$ rate will be dependent on the large change of the activation energy. Using our method, it is possible to solve numerically for the ET rate when the potential wells have different curvatures.

Table 1. Comparison of $k_{12}$ with $k_{n a}^{T S T}, k_{12}^{1 r r}$ and $k_{12}^{r e v}$

| $S=40, P=-10, T=300 \mathrm{~K}, \mathrm{~V}_{12}=10 \mathrm{~cm}^{-1}, \hbar \omega_{L}=100 \mathrm{~cm}^{-1}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $\lambda$ | $\mathrm{k}_{12}(\mathrm{sec}$ | $\mathrm{k}_{12}$ / | $k_{12} /$ | $\mathrm{k}_{12}$ |
| 10 | $2.34 \times 10^{9}$ | 0.95 | 0.97 | 0.98 |
| 50 | $9.76 \times 10^{7}$ | 0.99 | 0.994 | 0.997 |
| 100 | $2.45 \times 10^{7}$ | 0.9957 | 0.9978 | 0.999 |
| 200 | $6.13 \times 10^{6}$ | 0.9958 | 0.9969 | 0.9975 |
| 500 | $1.00 \times 10^{6}$ | 1.018 | 1.018 | 1.018 |
| $* k_{12}^{i r r}=k_{n a}^{T S T} k_{d i}^{A r r} /\left(k_{n a}^{T S T}+k_{d 1}^{A r r}\right)$, |  |  |  |  |
| $k_{12}^{\text {rev }}=k_{n a, 12}^{\text {TST }} /\left(1+k_{n a, 12}^{\text {TST }} / k_{d 1}^{\text {Arr }}+k_{n a, 21}^{\text {TST }} / k_{\text {d }}^{\text {Arr }}\right)$ |  |  |  |  |

Table 2. Comparison of $\mathbf{k}_{12}$ with $\mathbf{k}_{12}^{\mathbf{a p}}$
$T=300 \mathrm{~K}, \hbar \omega_{\mathrm{L}}=10 \mathrm{~cm}^{-1}, \mathrm{P}=-4, \lambda=10$

| S | $\mathrm{V}_{12}\left(\mathrm{~cm}^{-1}\right)$ | $\tau_{\mathrm{L}}(\mathrm{psec})$ | $\mathrm{k}_{12}\left(\mathrm{sec}^{-1}\right)$ | $\mathrm{k}_{12} / \mathrm{k}_{12}^{\mathrm{ap}}$ |
| :--- | :--- | :--- | :--- | :--- |
| 0.00948 | 0.1 | $100 / 3$ | 136 | 2.99 |
|  |  | $200 / 3$ | 68 | 2.99 |
| 0.0248 | 1.5 | $100 / 3$ | $2.72 \times 10^{7}$ | 2.82 |
|  |  | $200 / 3$ | $1.41 \times 10^{7}$ | 2.74 |
|  |  | 174 | 2.5 | $100 / 3$ |



Table 2 (cont'd)
$T=300 \mathrm{~K}, \hbar \omega_{\mathrm{L}}=10 \mathrm{~cm}^{-1}, \mathrm{P}=-4, \lambda=100$

| S | $\mathrm{V}_{12}\left(\mathrm{~cm}^{-1}\right)$ | $\tau_{\mathrm{L}}(\mathrm{psec})$ | $\mathrm{k}_{12}\left(\mathrm{sec}^{-1}\right)$ | $\mathrm{k}_{12} / \mathrm{k}_{12}^{\mathrm{ap}}$ |
| :--- | :--- | :--- | :--- | :--- |
| 0.00948 | 0.01 | $1000 / 3$ | 13.64 | 2.99 |
| 0.0166 |  | $2000 / 3$ | 6.83 | 2.99 |
|  | 0.375 | $1000 / 3$ | $7.41 \times 10^{4}$ | 2.97 |
|  |  | $2000 / 3$ | $3.88 \times 10^{4}$ | 2.88 |
| 0.039 | 0.788 | $1000 / 3$ | $1.50 \times 10^{7}$ | 1.06 |
|  |  | $2000 / 3$ | $7.67 \times 10^{6}$ | 1.04 |

$T=300 \mathrm{~K}, \hbar \omega_{\mathrm{L}}=100 \mathrm{~cm}^{-1}, \mathrm{P}=-4, \lambda=100$

| S | $\mathrm{V}_{12}\left(\mathrm{~cm}^{-1}\right)$ | $\tau_{\mathrm{L}}(\mathrm{psec})$ | $\mathrm{k}_{12}\left(\mathrm{sec}^{-1}\right)$ | $\mathrm{k}_{12} / \mathrm{k}_{12}^{\mathrm{p}}$ |
| :--- | :--- | :--- | :--- | :--- |
| 0.0753 | 0.01 | $100 / 3$ | 1.85 | 2.31 |
| 0.126 |  | $200 / 3$ | 0.93 | 2.31 |
|  | 1.0 | $100 / 3$ | $4.27 \times 10^{4}$ | 2.58 |
|  |  | $200 / 3$ | $2.27 \times 10^{4}$ | 2.69 |
| 0.313 | 7.5 | $100 / 3$ | $1.22 \times 10^{8}$ | 1.16 |
|  |  | $200 / 3$ | $6.25 \times 10^{7}$ | 1.14 |

* $k_{12}^{\mathrm{ap}}$ see eq. (3.19)

APPENDICES

## APPENDIX A

Formal derivation of reaction rate expression

We use a projection operator method to derive the formal reaction kernel and the reversible forward and backward reaction expression.

First, Laplace transformation (LT) of eq. (3.16) gives us
$\operatorname{s} \underline{\hat{\rho}}-\underline{\rho}(0)=[\underline{\underline{L}} \underline{\hat{\rho}}+\underline{k} \hat{\rho}]$
(AC)
where $\hat{\rho}$ is the $L T$ of $\left[\rho_{11}, \rho_{22}\right]^{T}$ and $\underline{\rho}$ ( 0 ) is the initial distribution. In our model, at $t=0$, the particle is distributed in potential well A, with an equilibrium distribution. For a harmonic potential this is a gaussian distribution. So $\underline{\rho}(0)=\left[g_{1}, 0\right]^{T}$, where $g_{1}=\exp \left(-\beta V_{11}\right) / \int \exp \left(-\beta V_{11}\right) d x$. Applying $\underline{E}, \underline{Q}$ to eq. (A1), we obtain
g $\underline{\underline{p}} \underline{\hat{\rho}}-\underline{p} \underline{\rho}(0)=-[\underline{p} \underline{\underline{L}} \underline{\underline{p}} \underline{\hat{\rho}}+\underline{p} \underline{\underline{q}} \underline{\underline{\rho}}+\underline{p} \underline{K} \underline{p} \hat{\rho}+\underline{p} \underline{K} \underline{Q} \hat{\rho}]$
(AC)
and
$\mathbf{Q} \underline{\underline{Q}} \underline{\hat{\rho}}-\underline{Q} \underline{\rho}(0)=-[\underline{Q} \underline{\underline{Q}} \underline{\underline{\rho}} \underline{\hat{\rho}}+\underline{Q} \underline{K} \underline{P} \underline{\hat{\rho}}+\underline{Q} \underline{\underline{Q}} \underline{\underline{\rho}}+\underline{Q} \underline{\underline{Q}} \underline{\underline{\rho}}]$
(AB)

Rearranging them, and using the following conditions,
$\underline{\underline{P}} \underline{\rho}(0)=\underline{\underline{g}} \int \mathrm{dx}\left[\begin{array}{l}\rho_{11}(0) \\ \rho_{22}(0)\end{array}\right]=\underline{\underline{g}}\left[\begin{array}{l}1 \\ 0\end{array}\right]=\left[\begin{array}{l}g_{1} \\ 0\end{array}\right] \quad$ (A.4a)
$\underline{\underline{Q}} \underline{\rho}(0)=(1-\underline{\underline{P}}) \underline{\rho}(0)=\left[\begin{array}{l}g_{1} \\ 0\end{array}\right]-\left[\begin{array}{l}g_{1} \\ 0\end{array}\right]=\left[\begin{array}{l}0 \\ 0\end{array}\right] \quad(A \cdot 4 b)$
where
$\rho_{11}(0)=g_{1}, \rho_{22}(0)=g_{2}$
$[\mathbf{s}+\underline{\mathbf{Q}}(\underline{\underline{L}}+\underline{\mathrm{K}})] \underline{\underline{Q}} \underline{\hat{\rho}}=-(\underline{\mathbf{Q}}+\underline{\mathbf{L}}+\underline{\mathbf{Q}} \underline{\underline{\mathrm{K}}}) \underline{\underline{\mathrm{P}}} \underline{\hat{\rho}}$,
then

$$
\begin{aligned}
& s \underline{\underline{p}} \underline{\hat{\rho}}-\underline{\underline{p}} \underline{\rho}(0) \\
& =-(\underline{\underline{L}} \underline{\underline{L}}+\underline{\underline{K}}) \underline{\underline{p}} \underline{\underline{\rho}}-\underline{P}(\underline{\underline{L}}+\underline{K}) \underline{\underline{Q}} \underline{\hat{\rho}} \\
& =-(\underline{\mathrm{P}} \underline{\underline{L}}+\underline{\mathrm{P}} \underline{\underline{K}}) \underline{\underline{P}} \underline{\hat{\rho}}+(\underline{\underline{p}} \underline{\underline{L}}+\underline{\underline{K}} \underline{\underline{K}})[\mathrm{s}+\underline{Q}(\underline{\underline{L}}+\underline{\underline{K}})]^{-1} \\
& \cdot(\underline{\underline{Q}} \underline{\underline{L}}+\underline{\underline{Q}} \underline{\underline{E}}) \underline{\underline{p}} \underline{\hat{\rho}} .
\end{aligned}
$$

Finally we have

$$
\begin{aligned}
& \left\{s+\left[\underline{\underline{P}}(\underline{\underline{L}}+\underline{\underline{k}})-\underline{\underline{P}}(\underline{\underline{L}}+\underline{\underline{E}})[s+\underline{Q}(\underline{\underline{L}}+\underline{\underline{E}})]^{-1}\right.\right. \\
& \underline{Q}(\underline{\underline{L}}+\underline{\underline{K}})]\} \underline{\underline{P}} \underline{\rho}=\underline{\mathrm{P}} \underline{\rho}(0) .
\end{aligned}
$$

Comparing this with eq. (3.7), we have

$$
\begin{aligned}
\underline{\underline{k}}= & \lim _{\substack{ \\
0}} \underline{\underline{g}}\left\{\underline{\underline{P}}(\underline{\underline{L}}+\underline{\underline{k}})-\underline{\underline{P}}(\underline{\underline{L}}+\underline{\underline{k}})[\mathrm{s}+\underline{\underline{Q}}(\underline{\underline{L}}+\underline{\underline{k}})]^{-1}\right. \\
& \underline{\underline{Q}}(\underline{\underline{L}}+\underline{\underline{k}})\} \underline{g} .
\end{aligned}
$$

Note that $\underline{\underline{P}} \underline{\underline{L}}=0$, as a boundary condition, and $\underline{\underline{E}}=0$, since $\underline{g}$ is the equilibrium distribution.

Our final formal result is
$\underline{\underline{k}}=\lim _{\boldsymbol{s} \rightarrow 0} \underline{\underline{g}}^{-1}\left\{\underline{\underline{P}} \underline{\underline{K}}-\underline{\underline{P}} \underline{\underline{K}}[\mathrm{~s}+\underline{\underline{Q}}(\underline{\underline{\mathrm{~L}}+\underline{K}})]^{-1} \underline{\underline{Q} \underline{\underline{K}}\}} \underline{\underline{g}} \quad\right.$ (AC)

To get the rate expression, we need to do the following expansion,
$\underline{\underline{k}}=\int d x\left[\underline{\underline{k}}-\underline{\underline{G}} \int d y \underline{\underline{G}}(x, y) \underline{\underline{Q}} \underline{\underline{k}}(y)\right] \underline{g}$
where
$\underline{G}(x, y)=[s+\underline{\underline{Q}}(\underline{\underline{L}}+\underline{\underline{E}})]^{-1}$
satisfies

$$
\underline{\underline{G}}=\underline{G}_{0}-\underline{G}_{0} \underline{\underline{G}} \underline{G}_{0^{\circ}}
$$

Then

$$
\begin{aligned}
& +\int d x \underline{K} \int d y \underline{G}_{0}(x, y) \underline{\underline{E}}(\underline{E}) \int d z \underline{G}_{0}(y, z) \underline{E} \underline{E}(z) \underline{E} \\
& \text { - ... } \\
& =\overline{\underline{K}}-\hat{\underline{K}} \overline{\underline{G}}_{0} \overline{\underline{K}}+\hat{\underline{K}} \underline{\underline{G}}_{0} \overline{\underline{K}} \hat{\underline{G}}_{0} \overline{\underline{K}}-\ldots \\
& =\left[1+\hat{\mathrm{K}} \underline{\underline{G}}_{0}\right]^{-1} \overline{\mathrm{~K}}, \\
& \text { (A.11) }
\end{aligned}
$$

where we have used

$$
\begin{aligned}
& \hat{\underline{K}}=\int d x \underline{\underline{K}}(x)=2 \int d x \operatorname{Re} K_{12}\left(x, x^{*}\right)\left[\begin{array}{rr}
1 & -1 \\
-1 & 1
\end{array}\right]=k\left[\begin{array}{rr}
1 & -1 \\
-1 & 1
\end{array}\right] \\
& \underline{\underline{G}}_{0}=\underline{G}_{0}-\int d y \underline{G}_{0}(x, y) \underline{g}(y) \\
& =\left[\begin{array}{ccc}
\mathbf{G}_{11}^{0}-\int G_{11}^{0} \mathbf{g}_{1} & 0 \\
& 0 & \\
& & G_{22}^{0}-\int G_{22}^{0} g_{2}
\end{array}\right] \\
& \overline{\mathrm{K}}=\int \mathrm{dx} \underset{\underline{K}}{\underline{\mathrm{~K}}}(\mathrm{x}) \underline{\mathrm{g}}(\mathrm{x}) \\
& =\left[\begin{array}{rr}
\bar{g}_{1} & -\bar{g}_{2} \\
-\bar{g}_{1} & \bar{g}_{2}
\end{array}\right], \bar{g}_{1}=2 \int d x \operatorname{Re} K_{12}\left(x, x^{*}\right) g_{1}, 1=1,2
\end{aligned}
$$

and

$$
\underline{k}=\left(1+k \bar{G}_{11}^{0}+k \bar{G}_{22}^{0}\right)^{-1}\left[\begin{array}{c}
1+k \bar{G}_{22}^{0} \\
k \bar{G}_{11}^{0} 1+k \bar{G}_{11}^{0}
\end{array}\right]\left[\begin{array}{r}
\overline{\mathrm{g}}_{1}-\overline{\mathrm{g}}_{2} \\
-\overline{\mathrm{g}}_{1} \\
\overline{\mathrm{~g}}_{2}
\end{array}\right]
$$

Finally,

$$
\begin{aligned}
k_{12} & =\left(1+k \bar{G}_{11}^{0}+k \bar{G}_{22}^{0}\right)^{-1} \bar{g}_{1} \\
& =k_{n a}^{12} /\left(1+k_{n a}^{12} / k_{d 1}+k_{n a}^{21} / k_{d 2}\right) \\
k_{21} & =\left(1+k \bar{G}_{11}^{0}+k \bar{G}_{22}^{0}\right)^{-1} \bar{g}_{2} \\
& =k_{n a}^{12} /\left(1+k_{n a}^{12} / k_{d 1}+k_{n a}^{21} / k_{d 2}\right) .
\end{aligned}
$$

## APPENDIX B

Derivation of $\mathbf{G}_{12}$

The potentials that we need are given in eq. (4.1). The crossing point can be calculated at $\mathrm{V}_{11}=\mathrm{V}_{22}$, 80
$\sigma=\frac{1}{2} x_{0}-v_{0} / k_{\omega} x_{0}$
and

$$
\begin{aligned}
v_{11}-v_{22} & =k_{\omega} x_{0}(x-\sigma) \\
& =\gamma(x-\sigma)
\end{aligned}
$$

where

$$
\gamma=k_{\omega} x_{0} .
$$

Assume the coupling term $\frac{V}{i \hbar}\left(\rho_{22}-\rho_{11}\right)$ is a source term then $G_{12}$ should satisfy the Fokker-Planck like equation

$$
\begin{align*}
& {\left[\frac{\partial}{\partial t}-D \frac{\partial^{2}}{\partial x^{2}}-\beta D\left(k_{\omega} x-\frac{1}{2} k_{\omega} x_{0}\right) \frac{\partial}{\partial x}-\beta D k_{\omega}+i \frac{\gamma}{h}(x-\sigma)\right]} \\
& G_{12}=\delta\left(x-x_{0}\right) \delta\left(t-t_{0}\right) . \tag{B.3}
\end{align*}
$$

## Use the space Fourier transformation,

$\int G_{12} e^{-18 x} d x=\hat{G}_{12}$
yields
$\left[\frac{\partial}{\partial t}+D s^{2}-\beta k_{\omega} D\left(-s \frac{\partial}{\partial s}-\frac{1}{2} x_{0} i s\right)+i \frac{\gamma}{h}\left(i \frac{\partial}{\partial s}-\sigma\right)\right] \hat{G}_{12}$
$=e^{-i \varepsilon x_{0}} \delta\left(t-t_{0}\right)$.

Now we want to calculate $\mathbf{G}_{12}$ from

$$
\begin{aligned}
& {\left[\frac{\partial}{\partial t}+\left(\beta k_{\omega} D s-\frac{\gamma}{h}\right) \frac{\partial}{\partial s}+\left(D s^{2}+i \frac{1}{2} \beta k_{\omega} D x_{0} s-i \frac{\gamma}{\hbar} \sigma\right)\right] \hat{G}_{12}} \\
& =0
\end{aligned}
$$

by solving the partial differential equation ${ }^{9}$.

## We use

$\frac{d \mathrm{t}}{1}=\frac{\mathrm{d} s}{\beta \mathrm{k}_{\omega} \mathrm{D} s-\frac{\gamma}{\hbar}}=\frac{\mathrm{d} \hat{\mathrm{G}}_{12}}{-\mathrm{D} \mathrm{s}^{2}-\mathrm{i} \frac{1}{2} \beta \mathrm{k}_{\omega} \mathrm{D} \mathrm{x}_{0} s+\mathrm{i} \frac{\gamma}{\hbar} \sigma} \quad(\mathrm{B} .6)$
and
1.
$\frac{d}{d}{ }^{d}=\beta k_{\omega} D s-\frac{\gamma}{h}$

$$
\begin{aligned}
& s-\frac{\gamma}{\beta k_{\omega} D \hbar}=c_{1} e^{\beta k_{\omega} D t} \\
& c_{1}=\left(s-\frac{\gamma}{\beta k_{\omega} D \hbar}\right) e^{-\beta k_{\omega} D t}
\end{aligned}
$$

2. 

$$
\begin{aligned}
\frac{d}{d} \ln \hat{G}_{12} & =-D s^{2}-i\left(\frac{1}{2} \beta k_{\omega} D x_{0} s-\frac{\gamma}{h} \sigma\right) \\
= & -D\left[c_{1} e^{\left.\beta k_{\omega} D t^{t}+\frac{\gamma}{\beta k_{\omega} D h}\right]^{2}}\right. \\
& -i\left[\left(\frac{1}{2} k_{\omega} \beta D x_{0}\right)\left(c_{1} e^{\beta k_{\omega} D t}+\frac{\gamma}{\beta k_{\omega} D h}\right)-\frac{\gamma}{h} \sigma\right]
\end{aligned}
$$

$$
\begin{aligned}
& \hat{G}_{12}=\hat{G}_{12}(t) \exp \left\{-D\left[c _ { 1 } ^ { 2 } \frac { 1 } { 2 \beta k _ { \omega } D } \left(e^{\left.2 \beta k_{\omega} D t-1\right)}\right.\right.\right. \\
& \left.+2 \frac{\gamma}{\beta k_{\omega} D h^{\prime}} c_{1} \frac{1}{\beta k_{\omega} D}\left(e^{\beta k_{\omega} D t^{t}-1}\right)+\left(\frac{\gamma}{\beta k_{\omega} D h^{\prime}}\right)^{2} t\right] \\
& -i\left[\left(\frac{1}{2} \beta k_{\omega} D x_{0}\right) c_{1} \frac{1}{\beta k_{\omega} D}\left(e^{\beta k_{\omega}}{ }^{D t}-1\right)\right. \\
& \left.\left.+\left(\frac{1}{2} \beta k_{\omega} D x_{0}\right) \frac{\gamma}{\beta k_{\omega} D h^{\prime}} t-\frac{\gamma}{h} \sigma t\right]\right\} .
\end{aligned}
$$

$$
\text { At } t=t_{0}=0
$$

$$
\hat{G}_{12}(0)=e^{-i s x_{0}}=\hat{G}_{12}^{0}(0)
$$

From

$$
\begin{aligned}
& s-\frac{\gamma}{\beta k_{\omega} D \hbar}=\left(s_{0}-\frac{\gamma}{\beta k_{\omega} D \hbar}\right) e^{\beta k_{\omega}}{ }^{D} t \\
& s_{0}=\left(s-\frac{\gamma}{\beta k_{\omega} D \hbar}\right) e^{\beta k} \omega^{D t}+\frac{\gamma}{\beta k_{\omega} D \check{K}} \\
& c_{1}=\left(s-\frac{\gamma}{\beta k_{\omega} D \text { h }}\right) e^{-\beta k_{\omega}}{ }^{t} \text {; }
\end{aligned}
$$

finally we have

$$
\begin{align*}
& \hat{G}_{12}=\exp \left\{-i x_{0}\left[\left(s-\frac{\gamma}{\beta k_{\omega} D h^{\prime}}\right) e^{-\beta k_{\omega} D t}+\frac{\gamma}{\beta k_{\omega} D \mathcal{h}}\right]\right. \\
& -D\left[\frac{1}{2 \beta k_{\omega} D}\left(8-\frac{\gamma}{\beta k_{\omega} D h}\right)^{2}\left(1-e^{-2 \beta k_{\omega} D t}\right)\right. \\
& +2 \frac{\gamma}{\left(\beta k_{\omega} D\right)^{2} h}\left(8-\frac{\gamma}{\beta k_{\omega} D K}\right)\left(1-e^{-\beta k_{\omega} D i}\right) \\
& \left.+\left(\frac{\gamma}{\beta k_{\omega} D K}\right)^{2} t\right] \\
& -i\left[\frac{1}{2} x_{0}\left(s-\frac{\gamma}{\beta k_{\omega} D \hbar}\right)\left(1-e^{-\beta k_{\omega} d i}\right)\right. \\
& \left.\left.+\frac{1}{2} \mathrm{x}_{0} \frac{\gamma}{\hbar} \mathrm{t}-\frac{\gamma}{h} \sigma \mathrm{t}\right]\right\} \text {. }
\end{align*}
$$

Inverting the Fourier transformation, we get

$$
\begin{aligned}
\hat{G}_{12} & =\frac{1}{2 \pi} \int \hat{G}_{12} e^{i s x} d s \\
& =\frac{1}{\sqrt{2 \pi}} \frac{1}{2 \sqrt{D \tau_{L}(1-\exp (-2 t))}} \exp \left\{\frac { 1 } { 2 } \left[2 D \frac{\gamma \tau_{L}^{2}}{h^{2}}\left(1-e^{-\bar{i}}\right)\right.\right.
\end{aligned}
$$

$$
\begin{aligned}
& \left.-i\left[x-x_{i} e^{-\bar{t}}-\frac{1}{2} x_{0}\left(1-e^{-\bar{t}}\right)\right]\right]^{2} /\left[D \tau_{L}\left(1-e^{-2 \bar{i}}\right)\right] \\
& \left.-D\left(\frac{\gamma \tau_{L}}{h}\right)^{2} \tau_{L} \bar{t}+i \frac{\gamma \tau_{L}}{h}\left(x-x_{i}-\frac{1}{2} x_{0} \bar{t}+\sigma \bar{t}\right)\right\} \quad(B \cdot 8)
\end{aligned}
$$

where $\overline{\mathrm{t}}=\mathrm{t} / \tau$.

$$
\begin{aligned}
& \left.-i\left[x-x_{i} e^{-\bar{t}}-\frac{1}{2} x_{0}\left(1-e^{-\bar{i}}\right)\right]\right]^{2} /\left[D \tau_{L}\left(1-e^{-2 \bar{t}}\right)\right] \\
& \left.-D\left(\frac{\gamma \tau_{L}}{h}\right)^{2} \tau_{L} \bar{t}+i \frac{\gamma \tau_{L}}{h}\left(x-x_{i}-\frac{1}{2} x_{0} \bar{t}+\sigma \bar{t}\right)\right\}(B .8)
\end{aligned}
$$

where $\bar{t}=t / \tau$.

## APPENDIX C

Eigen-functions of $\mathrm{L}_{12}$

The $\mathrm{L}_{12}$ operator with simplified notation is
$\left[\frac{\partial^{2}}{\partial x^{2}}+\left(x-\frac{1}{2} x_{0}\right) \frac{\partial}{\partial x}+1\right] \phi_{n}=\Lambda_{n} \phi_{n} \quad(C .1)$
with
$y=x-\frac{1}{2} x_{0}$.

The boundary condition at $x \rightarrow \pm \infty$ is $\phi_{n}=0$. Then the eigenvalue problem is

$$
\left[\frac{\partial^{2}}{\partial x^{2}}+\left(\frac{-1}{4} y^{2}+\frac{1}{2}-\Lambda_{n}\right)\right] \psi_{n}=0 \quad(C .2)
$$

where

$$
\phi_{n}=e^{-y^{2} / 4} \psi_{n}
$$

The solution is
$\Psi_{n}=\left(2^{n} n!\right)^{-1 / 2}\left(\frac{1}{2 \pi}\right)^{1 / 4} e^{-y^{2} / 4} H_{n}(y / \sqrt{2}) . \quad(C .3)$

So
$\phi_{n}=\left(2^{n} n!\right)^{-1 / 2}\left(\frac{1}{2 \pi}\right)^{1 / 4} e^{-y^{2} / 2} H_{n}(y / \sqrt{2})$

$$
\begin{equation*}
=r_{n} \tag{C.4}
\end{equation*}
$$

$\Lambda_{n}=-n, n=0,1,2, \ldots$.

The ground state, $n=0$, is $\left(\frac{1}{2 \pi}\right)^{1 / 4} e^{-\left(x-x_{0} / 2\right)^{2}}$.

## Adjoint operator

For an operator $L$ which satisfies
$L u=P_{0}(x) \frac{\partial^{2}}{\partial x^{2}} u+P_{1}(x) \frac{\partial}{\partial x} u+P_{2} u$,
then

$$
\begin{aligned}
\tilde{L} u & =\frac{\partial^{2}}{\partial x^{2}}\left(P_{0} u\right)-\frac{d}{d x}\left(P_{1} u\right)+P_{2} u \\
& =P_{0} \frac{\partial^{2}}{\partial x^{2}} u+\left(2 P_{0}^{\prime}-P_{1}\right) \frac{\partial}{\partial x} u+\left(P_{0}^{\prime \prime}-P_{1}^{\prime}+P_{2}\right) u .
\end{aligned}
$$

(C.6)

For our diffusion equation
$L_{12}=\frac{\partial^{2}}{\partial x^{2}}+x \frac{\partial}{\partial x}+1-\frac{\partial}{\partial t}$
$\tilde{L}_{12}=\frac{\partial^{2}}{\partial x^{2}}-x \frac{\partial}{\partial x}+\frac{\partial}{\partial t}$,
the left-hand eigen-function of $\mathrm{L}_{12}$ should be the right eigen-function of $\tilde{L}_{12}$.

Eigen-functions and eigen-values of $\tilde{\mathrm{L}}_{12}$

Let $\phi_{n}=e^{y^{2} / 4} \Psi_{n}$,
then $\tilde{L}_{12} \phi_{n}=\Lambda_{n}^{\prime} \phi_{n}$ is
$\left[\frac{\partial^{2}}{\partial y^{2}}+\left(\frac{-1}{4} y+\Lambda_{n}^{\prime}+\frac{1}{2}\right)\right] \Psi_{n}=0$,
where

$$
\begin{array}{ll}
\varphi_{n}=\left(2^{n} n!\right)^{-1 / 2}\left(\frac{1}{2 \pi}\right)^{1 / 4} e^{-y^{2 / 4}} H_{n}(y / \sqrt{2}) & (C \cdot 10) \\
\Phi_{n}=\left(2^{n} n!\right)^{-1 / 2}\left(\frac{1}{2 \pi}\right)^{1 / 4} H_{n}(y / \sqrt{2})=1_{n} & (C \cdot 11) \\
\Lambda_{n}^{\prime}=n, n=0,1,2, \ldots & (C \cdot 12)
\end{array}
$$

The identities that we use to derive the basis expansion are:
1.

$$
\begin{aligned}
& \mathbf{r}_{n}^{*} L_{12} r_{n}=\left(L_{12} r_{n}\right)^{*} r_{n} \\
& \Lambda_{n}=-\Lambda_{n}^{\prime}
\end{aligned}
$$

(C.13a)
(c. 13b )
2.

$$
\int_{-\infty}^{\infty} d x \mathbf{I}_{n}^{*} r_{n}=\delta_{m n}
$$

3. 

$$
\begin{equation*}
\frac{\partial}{\partial y} \phi_{n}=-\sqrt{n+1} \phi_{n+1}(y) \tag{C..13d}
\end{equation*}
$$

4. 

$$
\begin{equation*}
\int_{-\infty}^{\infty} f_{m}^{*} \frac{\partial}{\partial y} r_{n} d y=-\sqrt{n+1} \delta_{m, n+1} \tag{C..13e}
\end{equation*}
$$

5. 

$$
\int_{-\infty}^{\infty} 1_{m}^{*} y r_{n} d y=\sqrt{n+1} \delta_{m, n+1}+\sqrt{n} \delta_{m, n-1} \quad \text { (C.13f ) }
$$

6. 

$$
\int_{-\infty}^{\infty} \Phi_{n}(y) d y=\left\{\begin{array}{ll}
0 \\
(2 \pi)^{1 / 4}, & \text { for } n \geq 1 \\
n=0
\end{array} .\right.
$$

## APPENDIX D

## Vector recurrence relation

Eq. (4.8) can be written in the form

$$
\begin{equation*}
\frac{\partial}{\partial t} \underline{c}_{n}=\underline{Q}_{n}^{-} \underline{\underline{n}}_{n-1}+\underline{Q}_{n} \underline{c}_{n}+\underline{Q}_{n}^{+} \underline{c}_{n+1} \tag{D.1}
\end{equation*}
$$

where
$\underline{c}_{n}=\left[a_{n}^{+}, a_{n}^{-}, b_{n}^{+}, b_{n}^{-}\right]^{T}$
$\underline{Q}_{n}^{-}=\left[\begin{array}{lccc}0 & -\frac{1}{2} x_{0} \sqrt{n} & 0 & 0 \\ -\frac{1}{2} x_{0} \sqrt{n} & 0 & 0 & 0 \\ 0 & 0 & 0 & b \sqrt{n} \\ 0 & 0 & -b \sqrt{n} & 0\end{array}\right]$
$\underline{Q}_{n}=\left[\begin{array}{cccc}-n & 0 & 0 & 0 \\ 0 & -n & 0 & -a \\ 0 & 0 & -n & -b \sigma_{y} \\ 0 & \frac{1}{4} a & b \sigma_{y} & -n\end{array}\right]$
$\underline{Q}_{-}^{+}=\left[\begin{array}{cccc}0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & b \sqrt{n+1} \\ 0 & 0 & -b \sqrt{n+1} & 0\end{array}\right]$.

Let $\underline{c}_{n}(t)=\hat{c}_{-n} e^{-\Lambda t}$; we have
$\underline{Q}_{n}^{-} \hat{\underline{c}}_{n-1}+\left(\underline{Q}_{n}+\Lambda I\right) \hat{\underline{c}}_{n}+\underline{Q}_{n}^{+} \hat{\underline{c}}_{n+1}=0$.

We define
$\hat{\underline{c}}_{n \pm 1}=\hat{\underline{S}}_{\mathbf{n}}^{ \pm} \hat{\underline{c}}_{\mathbf{n}} ;$
then
$\underline{\underline{Q}}_{n}^{-} \hat{\underline{C}}_{n-1}+\left[\left(\underline{\underline{Q}}_{n}+\Lambda \mathbf{I}\right)+\underline{\underline{Q}}_{n}^{+} \hat{\underline{S}}_{n}^{+}\right] \hat{\underline{C}}_{n}=0$
or
$\left[\underline{\underline{Q}}_{n}^{-} \hat{\underline{S}}_{n}^{-}+\left(\underline{\underline{Q}}_{n}+\Lambda I\right)\right] \hat{\underline{c}}_{n}+\underline{\underline{Q}}_{n}^{+} \hat{\underline{c}}_{n+1}=0$.
(D.4b)

From eq. (D.4b)

$$
\begin{equation*}
\left[\underline{Q}_{n}^{-} \hat{\underline{S}}_{n}^{-}+\left(\underline{Q}_{n}+\Lambda \underline{I}\right)\right] \hat{\underline{c}}_{n}=-\underline{Q}_{n}^{+} \hat{\underline{c}}_{n+1} \tag{D.Fa}
\end{equation*}
$$

$\left[\underline{Q}_{n}^{-} \hat{\underline{S}}_{n}^{-}+\left(\underline{Q}_{n}+\Lambda I\right)\right] \hat{\underline{S}}_{n+1}^{-} \hat{\underline{c}}_{n+1}=-\underline{\underline{Q}}_{n}^{+} \hat{\underline{c}}_{n+1}$,
we have

$$
\begin{align*}
& \hat{\underline{S}}_{n}^{+}=-\left[\left(\underline{Q}_{n+1}+\Lambda 1\right)+\underline{Q}_{n+1}^{+} \hat{S}_{n+1}^{+}\right]^{-1} \underline{Q}_{n+1}^{-}  \tag{D.6a}\\
& \hat{S}_{n}^{-}=-\left[\underline{\underline{Q}}_{n-1}^{-} \hat{\underline{S}}_{n-1}^{-}+\left(\underline{Q}_{n-1}+\Lambda \mathbf{I}\right)\right]^{-1} \underline{Q}_{n-1}^{+} \tag{D.Wb}
\end{align*}
$$

$$
\begin{aligned}
& \hat{\underline{\underline{S}}}_{n}^{+}=-\left\{\left(\underline{\underline{Q}}_{n+1}+\Lambda I\right)+\underline{\underline{Q}}_{n+1}^{+}(-1)\left[\left(\underline{\underline{Q}}_{n+2}+\Lambda I\right)+\ldots\right]^{-1}\right. \\
&\left.\underline{\underline{Q}}_{n+2}^{-}\right\} \underline{\underline{Q}}_{n+1}^{-}
\end{aligned}
$$

and

$$
\begin{aligned}
& \hat{\underline{S}}_{0}^{-}=0 \\
& \hat{\underline{S}}_{1}^{-}=-\left[\underline{Q}_{0}+\Lambda I\right]^{-1} \underline{Q}_{0} \\
& \hat{\underline{S}}_{2}^{-}=-\left[\underline{Q}_{1}+\Lambda I+\underline{Q}_{1}^{-} \times(-1)\left(\underline{Q}_{0}+\Lambda I\right)^{-1} \underline{Q}_{0}^{+1}\right]^{-1} \underline{Q}_{1}
\end{aligned}
$$

$$
\vdots
$$

Our equation can be expressed in terms of $\hat{S}_{n}^{+}, \hat{S}_{n}^{-}$as

$$
\left[\left(\underline{\underline{Q}}_{n}^{-} \hat{\underline{S}}_{n}+\underline{\underline{Q}}_{n}^{+} \underline{\underline{S}}_{n}^{+}\right)+\left(\underline{\underline{Q}}_{n}+\Lambda \mathbf{1}\right)\right] \hat{\underline{c}}_{n}=0 \quad \text { (D.9) }
$$

ie.

$$
\begin{equation*}
\left[\underline{\underline{Q}}_{n}+\Lambda I+\underline{\underline{G}}_{n}(\Lambda)\right] \hat{\underline{c}}_{n}=0 \tag{D.10}
\end{equation*}
$$

where

$$
\hat{\underline{E}}_{n}(\Lambda)=\underline{\underline{Q}}_{n}^{-} \hat{\underline{S}}_{n}^{-}+\underline{Q}_{n}^{+} \hat{\underline{S}}_{n}^{+} .
$$

The eigen-value $\wedge$ can be determined from
$\operatorname{Det}\left[\underline{\underline{Q}}_{n}+\Lambda \mathbf{I}+\underline{\underline{G}}_{n}(\Lambda)\right]=0$.

For the zeroth block, $n=0$,

$$
\begin{equation*}
\operatorname{Det}\left[\underline{\underline{Q}}_{0}+\Lambda I+\underline{\underline{E}}_{0}(\Lambda)\right]=0 \tag{D.12}
\end{equation*}
$$

The structure of $\hat{K}_{0}$ is

$$
\left[\begin{array}{llll}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
k_{31} & k_{32} & k_{33} & k_{34} \\
k_{41} & k_{42} & k_{43} & k_{44}
\end{array}\right] .
$$

So

$$
\operatorname{Det}\left[\underline{\underline{Q}}_{0}+\wedge I+\underline{\underline{G}}_{0}(\Lambda)\right]
$$

$$
=\Lambda\left[\Lambda\left(\Lambda+k_{33}\right)\left(\Lambda+k_{44}\right)-a k_{32}\left(b \sigma_{y}+k_{43}\right)\right.
$$

$$
\left.+a\left(\frac{a}{4}+k_{42}\right)\left(\Lambda+k_{33}\right)-\Lambda\left(k_{34}-b \sigma_{y}\right)\left(b \sigma_{y}+k_{43}\right)\right]
$$

$$
\begin{equation*}
=0 \tag{D.13}
\end{equation*}
$$

This shows there is at least one $\Lambda=0$ root.

How are $\mathbf{k}_{12}$ and $\mathbf{k}_{21}$ determined?

First note that

$$
\begin{aligned}
\underline{v}(t) & =\left[\begin{array}{c}
a_{0}^{+} \\
a_{0}^{-} \\
\vdots \\
\cdot
\end{array}\right](t)=\underline{M} \underline{v}(0) \\
& =c_{0}\left[\begin{array}{l}
R_{0} \\
R_{0} \\
\vdots \\
\vdots
\end{array}\right]_{0}^{+\sum_{j=1}^{\infty} c_{j}\left[\begin{array}{c}
R_{0} \\
R_{1} \\
\vdots \\
\vdots
\end{array}\right]_{j} e^{-\Lambda_{j} t}}
\end{aligned}
$$

From probability conservation

$$
a_{0}^{+}(t)=(2 \pi)^{-1 / 4}
$$

i.e.

$$
\begin{equation*}
c_{0} R_{0,0}+\sum_{j=1}^{\infty} c_{j} R_{0, j} e^{-\Lambda_{j} t}=(2 \pi)^{-1 / 4} \tag{D.15}
\end{equation*}
$$

As $t \rightarrow \infty$,

$$
c_{0} R_{0,0}=(2 \pi)^{-1 / 4}
$$

so

$$
c_{0}=(2 \pi)^{-1 / 4} / R_{0,0^{\circ}}
$$

We need $C_{0} R_{1,0}=(2 \pi)^{-1 / 4} R_{1,0} / R_{0,0}$ to calculate $a_{0}^{-}(t)$. From $\left[\underline{\underline{Q}}_{0}+\Lambda I+\hat{\underline{G}}_{0}(0)\right] \hat{\underline{c}}_{0}=0$, for the first eicen-value $\Lambda=0$,

$$
\left[\begin{array}{lccr}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
k_{31} & k_{32} & k_{33} & k_{34}-b \sigma_{y} \\
k_{41} & k_{42}+\frac{a}{4} & k_{43}+b \sigma_{y} & k_{44}
\end{array}\right]\left[\begin{array}{l}
R_{0,0} \\
R_{1,0} \\
R_{2,0} \\
R_{3,0}
\end{array}\right]=0 .(D .17)
$$

Solving these algebraic equations yields

$$
\begin{align*}
R_{1,0} / R_{0,0}= & {\left[\frac{a}{4}+k_{42}-\frac{k_{32}}{k_{33}}\left(b \sigma_{y}+k_{43}\right)\right]^{-1} } \\
& {\left[\frac{k_{31}}{k_{33}}\left(b \sigma_{y}+k_{43}\right)-k_{41}\right] . } \tag{D.18}
\end{align*}
$$

So

$$
\begin{align*}
& k_{12}+k_{21}=\Lambda_{1}  \tag{D.19}\\
& \frac{2 k_{21}}{\Lambda_{1}}-1=R_{1,0} / R_{0,0} \tag{D.20}
\end{align*}
$$

Our final results are

$$
\begin{align*}
& k_{21}=\left(\frac{R_{1,0}}{R_{0,0}}+1\right) \Lambda_{1} / 2  \tag{D.21a}\\
& k_{12}=\Lambda_{1}-k_{21^{\circ}} \tag{D.21b}
\end{align*}
$$

## LIST OF REFERENCES

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