THEORY OF CHARGE TRANSFER REACTIONS IN CONDENSED MEDIA

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CERTIFICATE

Certified that the work presented in this thesis is based on the bonafide work done by Mr. P. Ananthapadmanabhan, under my guidance in the Department of Applied Chemistry, Cochin University of Science and Technology and that no part thereof has been included in any other thesis submitted previously for the award of any degree.

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Cochin - 22,
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PREFACE

The work embodied in this thesis was carried out in the Department of Applied Chemistry, Cochin University of Science and Technology. The study was confined to theoretical investigation of the dynamics of electrochemical charge transfer reactions.

The charge transfer reactions in condensed media-electron or proton transfer- between a solvated molecule and a macroscopic solid body such as electrode or membrane, has attracted the attention of many scientists, since the beginning of this century. A large number of papers related to theoretical as well as experimental investigations in this field, have been published during the past few years.

In the introductory chapter of this thesis, the work done on the charge transfer processes is reviewed. In this emphasis is given to the theoretical work done on the charge transfer reactions at a metal electrode-electrolyte interface.

The understanding of experimental observations in the electrochemical charge transfer reactions needs a knowledge of the theory for the process. Various theoretical approaches have been given for the electrochemical electron and proton transfer reactions. A brief account of this is given in chapter II.

The dynamics of the electrochemical electron transfer reactions have been studied by many authors. In this process the solvent has an important role in determining the dynamics of the process. In chapter III, a theoretical treatment developed for studying the dynamics of an electrochemical electron transfer reaction in the adiabatic limit is presented. It is argued that in the adiabatic limit, only the shift of the ionic orbital, due to its interaction with solvent molecules is important, and hence the shift may be taken as the reaction co-ordinate. Using the path integral technique, it is shown that the shift obeys a stochastic integral equation. This integral equation is converted into a random differential equation and this is then anlaysed to find the rate of the process.

Another process investigated is the electrochemical proton transfer reaction. The dynamics of this process has also been a subject of several papers. In chapter IV, theoretical approach for calculating the rate of the process, in adiabatic and non-adiabatic limits, is presented. Non-adiabaticity is accounted for by taking electronic excitations in the metal into consideration. As is well known, these electronic excitations obey boson statistics approximately. Therefore we make use of a bosonisation technique to map the problem of proton transfer, to a problem involving harmonic oscillators, after which the rate is calculated using the usual quantum transition state theory.

In the concluding chapter, brief summary our work is presented.

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APPENDIX B.

CHAPTER I

CHARGE TRANSFER REACTIONS IN CONDENSED MEDIA

(1) INTRODUCTION

An understanding of charge transfer reactions in condensed media, particularly that of electron transfer and proton transfer - be it homogeneous or heterogeneous, is of great chemical and biological interest[1-17]. Electron transfer is important in reaction mechanisms and photosynthesis, in disease control and energy transduction, in catalysis and copy machines, whereas proton transfer is important in acid-base catalysis, corrosion, electrocatalysis and industry (e.g.industrial production of heavy water). Of particular importance to the chemist is the charge transfer at the electrode-electrolyte interface. The kinetics of homogeneous and heterogeneous charge transfer reactions have a number of common characteristics. These include, the activation (Arrhenius) dependence of the process rate on the temperature and the presence of the correlation between the energy (or free energy) of activation and heat (or free energy) of reaction. Likewise, there are differences between these two, the reason being the involvement of the continuous electronic energy spectrum of the electrode in the heterogeneous charge transfer reactions.

Even though electrochemical charge transfer processes have been investigated for a long time, there still remain many things that are not understood properly. The role played by the solvent in determining the dynamics of the process is still a field of active investigation, even though its role in the energetics of the process is fairly well understood.

Another important aspect of the process, on which there have been very few investigations is the fact that if the charge transfer is at the surface of a metal electrode, the electronic system of the metal, with its continuum of allowed energy levels may play an important role in the process. This is particularly true of proton transfer reactions where there is significant interaction between the proton and the metal.

Thus, the characterization of non-radiative, heterogeneous charge transfer process involving the electrode (metal, semiconductor) and a solvated microspecies (ionic, molecular, inorganic/organic complexes) is currently one of the little understood problems in electrochemistry.

(2) ELECTROCHEMICAL ELECTRON TRANSFER REACTIONS

(2.a) HISTORICAL SURVEY

An essential aspect of electron transfer reactions is the change in the equilibrium nuclear configuration of an ion or molecule that results from its gain or loss of an electron. In the case of a metal complex in a polar solvent, this involves change in the metal-ligand and intraligand bond lengths and angles as well as changes in the vibrations and orientations of the surrounding solvent dipoles. As first noted by Libby in 1952[18], the coupling of the electron transfer to these nuclear configuration changes is governed by energy and momentum conservation requirements as expressed in the Frank-Condon principle. According to this principle, internuclear distances and nuclear velocities do not change during an electronic transition; in other words, electron transfer occurs at essentially constant nuclear configuration and momentum. This requirement is central to classical as well as quantum mechanical electron transfer theories. In the classical theories, use is made of an activated complex formalism in which the electron transfer occurs at the intersection of two potential energy surfaces - one for the reactants and the other for the products. The Frank-Condon principle is obeyed since the nuclear configuration and energies of the reactants and products are the same at the intersection. In the quantum mechanical theories, on the other hand, the intersection of potential energy surfaces is deemphasized, nuclear tunneling from the initial to the final state is allowed for, and the electron transfer is treated as a radiationless transition between the reactant and product states. The fitness of a particular nuclear configuration for electron transfer is related to the square of the overlap of the vibrational wave functions of the reactants and products (i.e.to the Frank-Condon factors of the transition).

The early electron transfer theories were non-adiabatic[18-21], that is, the rate constant depended explicitly on the electronic interactions of the reactants and the nuclear configuration change was not specifically calculated[19,21]. A few years later Marcus published the first of a series of papers on classical (activated-complex) electron transfer theory. In his papers[22-25], the electron transfer was assumed to be adiabatic; that is, the electronic interaction was taken to be large enough so that it no longer determined the rate of the reaction. The reaction would occur as soon as the critical configuration is attained. So the rate is independent of electronic interactions. Intramolecular configuration changes were neglected and the solvent configuration change was treated classsically, using concepts developed for discussing charge transfer spectra[26]. Reactions with and without free energy changes were treated. This model did not account for the important fact that despite the similarity of the solvent configuration changes, the rates of electron exchange between +2 and +3 ions spanned many orders of magnitude. This result indicated the importance of the detailed electronic configuration of the reactants and products in determining electron transfer rates.

In 1957, Marcus[27] gave the results of a numerical calculation of the electron transfer barriers in the $Co(H_2O)_6^{2+}$-$Co(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{2+}$-$Fe(H_2O)_6^{3+}$ exchange reactions, which included contribution from intramolecular configuration changes. Calculations involving the intramolecular configuration changes were published by George and Griffith[28] in 1959. Such expressions were extended to reactions with net free energy changes by Marcus[29-32] and Hush[33,34] and were generalized to include electrochemical[25,35,36] and mixed-valence systems[34]. A semiclassical formalism, in which the classical expression for the intramolecular configuration changes were corrected for nuclear tunneling effects, was introduced in 1962[37]. In parallel with these developments, Levich[38-40] and Dogonadze[41,42] published a quantum mechanical description of the solvent configuration change in which first order time-dependent perturbation theory was used to describe the time evolution of the initially prepared zero order states. This represented the first detailed treatment of non-adiabatic electron transfer reactions.

In the 1970s various quantum mechanical aspects of the electron transfer problem were treated in detail[43-52] and *ab initio* molecular orbital calculations of exchange rates were initiated[53,54]. Major advances in the application of radiationless transition formalism to electron transfer process were made, culminating in an elegant treatment in which the electron donor, electron acceptor and the surrounding solvent were treated as a `supermolecule'[55]. Much of the theoretical work of this period was directed towards explaining the distance and temperature dependence of electron transfer processes in biological systems[56-65]. At the same time, experimental evidence indicated the need for the revision to the classical and quantum mechanical treatment of highly exothermic reactions. Although, there has been much discussion of this problem and much progress has been made[46,55,66-68] some questions regarding the theories remained unsolved. A major shortcoming of the quantum mechanical treatment is that it does not account for large entropies of reaction. To overcome this, the solvent reorganization (free energy) expressions of Marcus are generally used.

Despite the shortcomings of the theories in the highly exothermic region, there is general agreement concerning the treatment of thermoneutral and moderately exothermic electron transfer reactions. Sutin[69] has given a description of this type of reactions in weakly interacting systems, taking $Fe(H_2O)_6^{2+}$ -$Fe(H_2O)_6^{3+}$ exchange reaction, as an example.

Recently, the dynamical role of the solvent for the electron transfer reactions occuring in the solution, be it homogeneous or heterogenous, has been the subject of many papers[70-116]. Much theoretical as well as experimental investigations of the solvent effect on electron transfer processes have been made. Towards the theoretical approach, Marcus *et al*[73,80,81,84,88,113,130,131], Levich, Dogonadze and Kuznetsov (LDK)[75,79,86,89,90], Sutin *et al*[72], Jortner *et al*[96,99,109], Zusman[116], Calef and Wolynes[70,71,92,93], Mikkelsen and Ratner[78.83,124] have made contributions whereas experimental investigations were made by Weaver *et al*[91,96,97,99-107,109-111] and Foss *et al*[87,115]. Mikkelsen and Ratner[83], in their review, have clearly given the important differences between the solid-phase and solution-phase electron transfer reactions.

During the course of these theoretical investigations a number of stimulating qualitative proposals of a more chemical nature were made. One of the major developments was the demonstration by Taube and Myers[117] and by Halpern[118] and their coworkers - that in certain cases, electron transfer from the initial to final state occurs in multiple steps, involving intermediate states belonging to a bridged species. Such a multi-step process becomes important when the coupling between the donor and acceptor orbitals is vanishingly small or when the direct transition is forbidden due to symmetry constraints. In the former case, the bridging orbitals may couple more successfully with the acceptor and donor orbitals and thus provide a favourable path for electron transfer reaction to occur. The resulting catalytic effects of bridging species have been observed in both homogeneous and heterogeneous electron transfer reactions[119].

A theory for bridge assisted electron transfer reactions, both homogeneous and heterogeneous, has been developed by Dogonadze *et al*[120-123] for a case where bridging species has a continuous distribution of energy levels. Two mechanisms for electron transfer viz (i) push-pull, in which the electron is first trasferred from the initial state to bridge and thereafter, from bridge to the final state and (ii) pull-push, wherein the transfer of electron from bridge to final state create a vacancy in the bridge which is filled at a later stage by an electron occupying the initial stage, have been investigated by these authors. A detailed account of theoretical treatments of homogeneous and heterogeneous bridge assisted electron transfer has been given by Mishra and Rangarajan[77].

Recently, Hush *et al*[125-129] has made theoretical and experimental investigations of bridge-assisted electron transfer on a series of metal complexes. A nonsuperexchange coherent mechanism for homogeneous bridge-asssisted electron transfer reactions has been proposed by Marcus and Almeida[130,131]. The authors assume a strong electronic coupling between the bridge and donor species so that the entire transfer from the donor to bridge-acceptor couple systems occurs coherently rather than incoherently, in two successive steps and the transfer is treated non-adiabatically.

(2.b) ADIABATIC AND NON-ADIABATIC REACTIONS [30,77,132]

A reaction is said to be adiabatic when the reacting system moves during the whole course of the reaction along the same potential energy curve corresponding to the given electronic state (curve a in Figure I.1). A non-adiabatic reaction is one in which the reacting system undergoes transitions during the course of the reaction from one potential energy curve to another corresponding to a higher energy electronic state of the activated complex (curve b in Figure I.1).

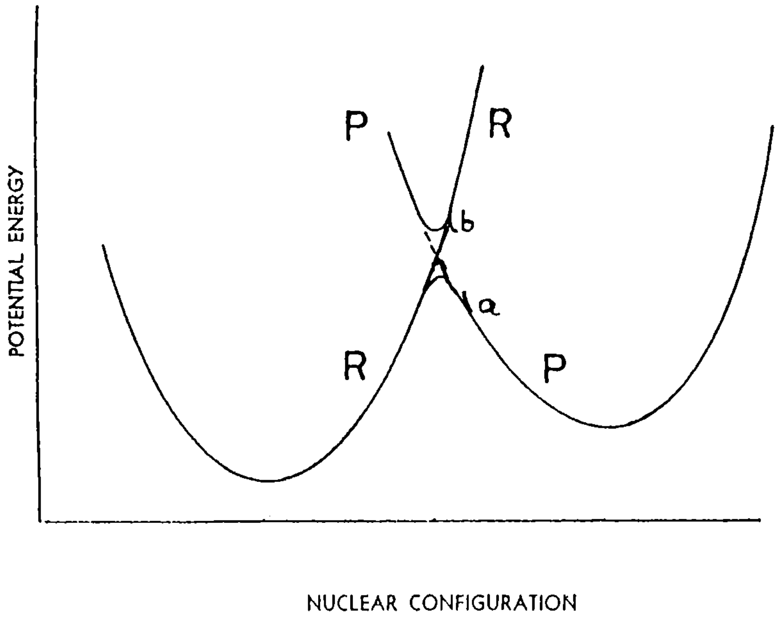

Fig. I.1. Profile of potential energy surface of reactants (R) and that of products (P), plotted versus nuclear configuration of all atoms. Arrow a represents adiabatic and b represents non-adiabatic motion in the region of closest approach of two potential energy surfaces.

According to the transition state theory (TST) formalism, these two types of reactions influence the value of transmission coefficient, $\varkappa$, which is a part of the pre-exponential term in the absolute rate expression. The value of $\varkappa$ is unity for an adiabatic reaction and less than unity for a non-adiabatic reaction.

In the adiabatic case, due to the strong interaction of the reactants at their closest approach the gap between the lower and higher potential energy curves will increase. So during the course of whole reaction, the system will follow the lowest potential energy surface and the probability of transition to the upper curve will become small. The reverse is the case for the non-adiabatic reaction.

The distinction between the adiabatic and non-adiabatic reactions can be clarified by applying semiclassical Landau-Zener theory[133,134] for the transition probability of the reacting system from the lower electronic state to the upper one. According to them, the probability of transition from the reactant to the product state is determined by the factors like relative velocity of approach of the one reactant to the other during the reaction and the electronic interaction between them.

This is the case of homogeneous reactions. For heterogeneous electron transfer reactions, the mechanism of electron transfer is the same, but the potential energy surface is to be modified. For e.g. for electrode reaction[135,136], the potential energy surface is as shown in figure.I.2.

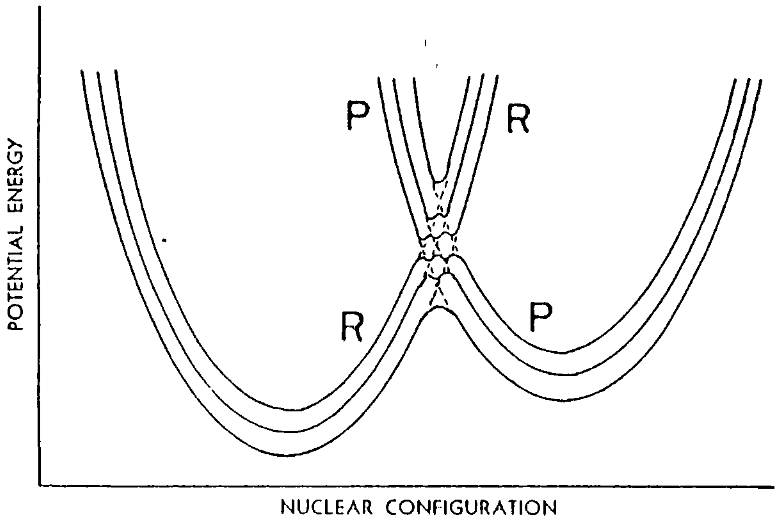

Fig.I.2. Profile of potential energy surface of reactants (R) and that of products (P), plotted versus nuclear configurations of all atoms, for an electrode reaction. Only three of the numerous electronic energy levels of this system are indicated.

Each surface in the figure I.2 is a many electron energy level of entire reacting system and is a function of nuclear co-ordinates. The different R - surfaces differ only in the distribution of these electrons among the `one electron quantum states'in the metal. The different P - surfaces differ in a similar way from each other. The unperturbed surfaces are drawn parallel since their energy differences are relatively unaffected by many of the usual changes of nuclear co-ordinates (those related to bond-lengths of the reactants and solvent orientation). It has been a difficult problem to treat the dynamics on such a continuum of surfaces, and a solution to this is the bosonization technique[135].

(2.c) OUTER AND INNER SPHERE ELECTRON TRANSFER REACTIONS

Electron transfer reactions can be classified as outer sphere and inner sphere reactions[136,137] depending on (i) changes occuring in the reactant configuration during electron transfer process and (ii) the time constants associated with these changes viz a viz charecteristic time scale for electron transfer step.

Outer sphere electron transfer reaction occurs with only little distortion of chemical bonds during electron transfer step, though there can be subsequent relaxation in the reactant configuration. The theoretical analysis of this type of reaction is easy, since in the time axis, the elementary electron transfer step can be decoupled from the accompanying relaxation in the reactants. Also, assuming the electron transfer step to be the rate determining step, one can concentrate on the theoretical description of this step alone, with due consideration to the modulations caused by the longitudinal polarization modes of the solvent medium. On the other hand, elementary electron transfer step and the change in the bond characteristics of reactants can occur `simultaneously' in an inner sphere mechanism, and therefore, dynamics of these two processes cannot be separated, thus making the theoretical analysis of inner sphere processes difficult.

Basically, in the inner sphere electron transfer reactions, in contrast to outer sphere reactions wherein the inner shell constituents are considered to be frozen, intramolecular dynamics leading to changes in bare, reactant-ligand and intraligand bond lengths, and bond angles need to be considered. These configurational changes are expected to manifest[1] as (i) a higher experimental activation energy in comparison to outer sphere processes (ii) a marked temperature dependence of activation energy (iii) a deviation from the Gaussian dependence of the rate expression in endothermic and exothermic reactions and (iv) a contribution from inner sphere modes to both pre-exponential (i.e. quantum tunneling factor) and activation part of the rate expression whenever there is strong distortion and displacement in the intramolecular vibrational potential energy surface[137,138]. The theoretical treatments of inner sphere dynamics have been done by various authors[30,35,37,44,47,119,139-149].

A well known example for a homonuclear outer sphere electron transfer reaction is

$$MnO_4^{2-} + MnO_4^{-} \longrightarrow MnO_4^{-} + MnO_4^{2-} \qquad (1)$$

which can be followed by isotopic substitution or by NMR line broadening of the central manganese atom. During this process the coordination sphere remains intact and the overall process is controlled by electron transfer.

An example of a heteronuclear outer sphere electron transfer reaction is

$$[Fe(CN)_6]^{4-} + [IrCl_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{4-} \qquad (2)$$

which is thus accompanied by a net chemical change.

A heteronuclear inner sphere electron transfer reaction is

$$[(NH_3)_5CoCl]^{2+} + [Cr(H_2O)_6]^{2+} + 5\,H_2O \longrightarrow [Co(H_2O)_6]^{2+}$$
$$+ [Cl\ Cr(H_2O)_5] + 5\,NH_3 \,. \qquad (3)$$

Here reaction proceeds via an intermediate binuclear complex of the form $[(NH_3)_5\ Co\ Cl\ Cr(H_2O)_5]^{4+}$. The actual charge transfer in the above equation (3) is thus preceded and succeeded by ligand substitution.

A case of inner sphere electron transfer reaction without ligand transfer is the reduction of hexachloroiridate(IV) by acquochromium(I)

$$IrCl_6^{2-} + Cr(aq)^{2+} \longrightarrow [Cl_5Ir\ Cl\ Cr(H_2O)_5] \longrightarrow IrCl_6 + Cr(aq)^{3+}. \qquad (4)$$

(3) HOMOGENEOUS VS ELECTROCHEMICAL CHARGE TRANSFER REACTIONS

The reaction with charge transfer include the transport of electron or proton. An example for homogeneous electron transfer reaction is the redox reaction,

$$[Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \qquad (5)$$

and for heterogeneous electron transfer reaction is the redox reaction at an electrode

$$[Fe(CN)_6]^{3-} + e^-(metal) \longrightarrow [Fe(CN)_6]^{4-} . \qquad (6)$$

Similarly for the homogeneous proton transfer reactions the acid-base reaction

$$A\ H^+ + B \rightleftharpoons A + B\ H^+ \qquad (7)$$

whereas for the heterogeneous proton transfer reaction, the hydrogen ion discharge at an electrode

$$H_3O^+ + e^-(metal) \longrightarrow H_{ads} + H_2O \qquad (8)$$

illustrates the examples for these types of reactions. In equation (8), H_{ads} indicates that the hydrogen atom chemisorbed on the metal surface.

There are several relations of fundamental importance that characterize the difference between chemical and electrochemical processes. In the electrochemical case, the reaction rate or the corresponding current density is experimentally variable not only through change of concentration or temperature as for an ordinary chemical reaction, but can additionally be modulated over a wide range by variation of electrode potential. In the chemical reactions, the velocity is determined by the probability of formation of an energetically activated state of the reactants, from which products are formed by redistribution of atoms or molecular arrangements which depends on the free energy of activation through Boltzmann's distribution function and Arrhenius law of chemical kinetics. Electrode reactions involve similarly a free energy of activation which, unlike chemical reactions, depends on the potential and so their rate also depends on the potential.

For homogeneous proton transfer reactions[150], the BrØnsted relation is valid while in the electrochemical case, the corresponding relation is the Tafel equation. In the electrochemical proton transfer reactions, the electronic energy can be varied by varying the potential whereas in the chemical reactions the acidity is varied. Both these relations have been verified experimentally[201].

(4) ELECTROCHEMICAL PROTON TRANSFER AND HYDROGEN EVOLUTION REACTION

(4.a) HISTORICAL SURVEY

Since the early days of electrochemistry, the electrochemical proton transfer and hydrogen evolution reaction (HER) has been one of the most comprehensively studied electrochemical processes. The HER provided the basis for the first report of Tafel law[151] at the beginning of this century, which gave the relationship between rate (current density, i) and the departure of the potential from the equilibrium, η as

$$i = A \exp(-\alpha F\eta/kT) \ . \qquad (9)$$

However Tafel's assumption was that the combination of hydrogen atoms on the surface was the slow step of HER and his neglect of consideration of the electron transfer step as rate determining has led to the calculation of incorrect value of transfer coefficient, α.

Smits[152] in 1922 suggested that slow discharge could be a rate determining step in HER. The first quantum mechanical theory of charge transfer was that of Gurney[153] in 1931. In the Gurney model, the product formed by the transfer of an electron to a proton was considered to be a hydrogen atom in water rather than a hydrogen atom bonded to the electrode. Calculation of the heat of activation on this basis gave values that were too high.

Butler[154] modified Gurney's mechanism to take into account bonding (chemisorption) of the product hydrogen atoms (in H_3O^++ electron ——> H_{ads}) to the metal. Horiuti and Polanyi[155] had pointed out the effect of metal-hydrogen bond upon the reaction rate. They did not consider the quantum mechanical aspects of electron transfer whereas Butler's model took both Gurney's ion quantum mechanical transfer and the effect of metal-hydrogen bond strength into account.

Parsons and Bockris[156] developed Butler's extension of the Gurney theory, with the assumption that the probability of electron transfer to the proton was unity at the crossing point at the col of the potential energy surfaces. They made rough numerical estimate of the rate of the proton discharge reaction under adiabatic electron transfer conditions.

The above developments of Gurney's model had not taken into account the quantum mechanical properties of the discharging proton. However, the quantum properties of protons at interfaces had been considered at early stages, by Bawn and Odgen[157] who calculated the rate of transition of a proton and deuterium across an Eckart Barrier. In homogeneous system, the quantum mechanical effects of protons have been considered by Bernal and Fowler[158] and Conway, Bockris and Linton[159]. Later, Christov[160-163] developed a detailed picture of quantum mechanical transfer of protons in several mechanistic interpretations of data on separation factors. Conway[164] showed that given certain assumptions concerning barrier width, proton tunneling in the hydrogen discharge reaction could affect markedly the Tafel slope and gives a potential dependence of separation factor.

Some calculations of the quantum mechanics of electrode reactions involving protons were carried out by Bockris and Matthews[165]. They calculated the effect of quantum mechanical penetration of protons through the classical barrier from the H_3O^+ ion (interacting with the surrounding water molecules) to the electrode. Neutralisation was asssumed to take place upon penetration of barrier.

Marcus[166] and Marcus and Cohen[167], discussed the possibility of calculating the chemical part of the energy of activated state for homogeneous proton transfer reaction by the bond energy-bond order (BEBO) method[168,169].

Levich, Dogonadze and his co-workers[43,170-172] have applied their electrostatic model to proton discharge[173] and homogeneous proton transfer[174]. German *et al*[175] has discussed the H/T separation factor on the basis of this model. In order to obtain a sufficiently high value of the separation factor, they find it necessary to abandon the adiabatic proton (or tritium) transfer and adopt a nonadiabatic model. The proton jump distance is considered potential dependent, as it involves an ion-electrode interaction. No quantitative calculation of separation factors from this approach have been published.

The LDK quantum mechanical model[173] for the proton transfer assumed the hydrogen atom in the adsorbed state is neutral. But detailed analysis of the dependence of the symmetry factor on the temperature and potential has led to the development of a new model, charge variation model (CVM)[181] in which the variation of the charge of the adsorbed hydrogen atom was assumed. Much theoretical and experimental work on electrochemical proton transfer reactions were done for the last few years[75,176-221]. Towards this, the contributions of Bockris *et al*[191,216], Conway *et al*[189,190,192-196,198,200,201,203,205,207,208,211-213], Krishtalik *et al*[177-179,206,220], Kuznetsov[75,181,182,187,188,210], Ulstrup[183], Frese Jr.[204], Schmickler[215]etc. are noteworthy. Conway in his review[201], gives the important theoretical as well as experimental observations on electrochemical proton transfer reactions.

(4.b) PROTON TUNNELING IN ELECTROCHEMICAL HYDROGEN EVOLUTION REACTION

The light particles such as electron, proton and to a certain extent deuteron can transmit through energy barriers by tunneling, in addition to their classical transition over such barriers by means of thermal activation[159,222]. Much kinetic work has been conducted to identify the process, but only a few examples have been found at sufficiently low temperatures where the rate through the classical thermal activation pathway is relatively much diminished in comparison with the rate of proton tunneling pathway. So the latter can be identified, when significant.

Experiments at low temperatures are therefore preferred for detection of proton tunneling since the classical and quantum mechanical tunneling process of proton transfer always occur as parallel reactions, with the relative contributions being determined by temperature and mass of the particle being transferred. Usually, the classical, thermally assisted transfer becomes the dominant process at elevated temperatues.

Attempts were made to find out the possibility of proton tunneling in HER[223] by conducting direct electrode kinetic and H/D kinetic isotopic effect measurements on the HER down to about 173K in methanolic HCl solution. Unfortunately, the experimental indication of proton tunneling in HER have been largely negative while special kinetic effects e.g. large and potential dependent Tafel slopes were shown to be expected theoretically if a proton tunneling pathway dominated. However, in some homogeneous chemical reactions involving proton transfer[159,224], evidence for significant proton tunneling has been found out.

The electrochemical H/D isotopic separation factor, S, is another quantity that has been examined with regard to proton tunneling effects. High values for S are expected on some models for significant proton tunneling, due to negative exponential dependence of tunneling transfer rates on mass of the particle. Again, clear indication of S being determined principally by tunneling are not found[222]. Theoretical study of proton tunneling in the electrochemical HER has been carried out by many authors. The difference in their analysis is mainly in the models of the potential barrier for proton tunneling, that they used[160-163,165,225-229].

(5) ACTIVATIONLESS AND BARRIERLESS PROTON DISCHARGE REACTIONS

The activation energy of an electrochemical reaction such as the H_3O^+ ions discharge depends on overpotential as

$$A = A_e - \alpha \eta F \qquad (10)$$

where A is the real activation energy at overpotential η, and A is the same quantity at the equilibrium potential.

Experiments show that the transfer coefficient α is constant in a certain range of potentials. In many cases it has a value close to 1/2.

The above equation (10) shows that the activaton energy of the discharge process decreases with an increase in the overpotential; On the other hand for the reverse reaction i.e. for the ionization reaction it increases.

$$A' = A_e' + \beta \eta F \tag{11}$$

It follows from thermodynamics that at a given potential for a one electron process, $\alpha + \beta = 1$.

For a cathodic proton discharge reaction, since the activation energy at a given potential is finite and decreases with increasing overvoltage, it vanishes for a sufficiently high overpotential. In this case, the reaction rate is the highest and a further increase in the potential will not lead to an increase in the current. In other words, $\alpha = 0$ for such an *activationless process.* For the reverse ionisation reaction at these potentials, $\beta = 1$.

In the other limiting case, i.e. decrease of overvoltage leads to an increase of the discharge activation energy, but at the same time also to a decrease in the actvation energy of ionisation. At a sufficiently low cathode potential, i.e. at a sufficiently high anode potential, the activation energy of ionisation vanishes. In this case $\beta = 0$ and $\alpha = 1$. The possibility of such a process was shown by Krishtalik[230] in 1960.

Unlike the activationless processes, the processes corresponding to $\alpha = 1$ (or $\beta = 1$) requires a considerable activation energy. But in contrast to the relationships for an ordinary discharge, this activation energy is equal to the heat of an elementary act of the reaction, since the activation energy of the reverse process is equal to zero. The potential diagram of the process does not contain the usual hump, activation barrier, and therefore such processes are called *barrierless*[230].

A detailed discussion of experimental and theoretical observations and explanations of these two processes is given by Krishtalik[231]. So far as theoretical treatments are concerned, no existing models can give a satisfactory explanation for the sharp change of symmetry factor (transfer coefficient) between normal and barrierless regions, in the range of potentials in which hydrogen evolution occurs.

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CHAPTER II

THEORY OF ELECTROCHEMICAL ELECTRON TRANSFER AND ELECTROCHEMICAL PROTON TRANSFER REACTIONS

(1) ELECTROCHEMICAL ELECTRON TRANSFER - DIFFERENT APPROACHES

Common to the most theoretical approaches[1-5] to the calculation of reaction rates are three assumptions. They are:(i) the microscopic states of configurations from which the system may undergo reaction (classically or quantum mechanically) are assumed to be in thermal equilibrium with the remaining states, (ii) the interaction of the electronic orbitals of the reactants and electrode is weak and (iii) a system having just undergone electron transfer goes on to form stable configurations of the products. For example, in classical calculations based on the crossing of surfaces in phase space, the rate is equated to the rate of first passages.

Common to all treatments[1-3] is the discussion in terms of potential energy surface and the importance of the crossing point of the reactant's surface with product's surface in determining the electron transfer probability.

The differences among the treatments range from minor to major. Some are developed from fundamental considerations, while others are less rigorous. Levich and Dogonadze[1] treat the polarization dynamics macroscopically but in an elegant fashion. They ignore, dielectric dispersion and any changes in the inner coordination shell. Hush[4] has formulated the problem in such a way that he could calculate the contribution of inner coordination shell from ion-dipole and ligand-field arguments.

The treatments may be classified, in part, with respect to the effects they include in their calculation of the probability of reaching the intersection surface. The probability appears via a free energy of reorganization term or via some equivalent term. These free energy terms may have contributions from (i) energy and entropy changes in the inner coordination shell due to changes in bond lengths and angles, (ii) changes in ion size due to changes in bond lengths causing thereby small changes in the solvation free energy of the medium outside the inner coordination shell and (iii) for any given size of ions in the activated complex, a change in the vibrational and orientation polarization at each point in the medium.

Based on these effects, various theoretical treatments have been given for the electrochemical electron transfer reaction.

(1.a) The Marcus Treatment for Homogeneous and Heterogeneous Electron Transfer

Marcus[2,6-10] uses a general classical statistical mechanical approach with the rate constant given by

$$K = \varkappa\ Z\ \exp(-\Delta G^{\ddagger}/RT) \qquad (1)$$

where $\varkappa$ is the electron transmission coefficient in the activated state, Z is the collision number for the reaction and $\Delta G^{\ddagger}$ is the free energy of activation. For the homogeneous case Marcus typically takes $Z = 2.5 \times 10^{11}\ M^{-1}\ sec^{-1}$ and for the heterogeneous case $Z = 10^{-4}$ cm sec^{-1}. The free energy of activation includes the following contributions.

$$\Delta G^{\ddagger} = \Delta G_i^{\ddagger} + \Delta G_o^{\ddagger} + \Delta G_w^{\ddagger} + \Delta G_e^{\ddagger} \qquad (2)$$

where $\Delta G_o^{\ddagger}$ and $\Delta G_i^{\ddagger}$ are the reorganizational free energy contributions from the outer and inner solvation spheres. $\Delta G_w^{\ddagger}$ is the work term associated with bringing the reacting ions together or to the electrode surface and $\Delta G_e^{\ddagger}$ corresponds to an entropy term associated with any change in the electronic multiplicities in the initial and final states.

Marcus assumes the electron transfer process to be only moderately adiabatic to the extent that the transmission coefficient $\varkappa$ is approximately unity but not so strongly adiabatic that the activated state has appreciable resonance stabilization. He uses non-equilibrium dielectric polarization theory involving continuum concepts to calculate $\Delta G_o^\ddagger$. The term $\Delta G_i^\ddagger$ is expressed in terms of vibrational contributions of the inner-solvation sphere to the partition function of the activated complex and the corresponding zero energies. The principal configurational changes in the inner sphere are the changes in bond length from the inner sphere solvent molecules to the central ion, and therefore $\Delta G_i^\ddagger$ is approximately equal to the difference of the zero-point energy of the breathing mode in the activated and initial states. The difference can be estimated from the force constants for breathing mode of the inner sphere in the initial and final states, as has been done by Marcus[6] and Sutin[11] or from the potential energy functions for the initial and final states[4,12].

For electrode reaction involving metals, Marcus assumes that the electronic energy levels of the metal contributing to the reaction are confined to within ±kT of the Fermi level. He then considers the distribution of activated complexes corresponding to radiationless electron transfer to or from various electronic energy levels in the metal to be equivalent to a single activated complex corresponding to the Fermi level. Contributions to $\Delta G_o^\ddagger$ arising from the action of the image forces in the metal on the solvent polarization are also taken into account.

One of the more important outcomes of Marcus treatment is the relationship between the heterogeneous electron transfer rate constant k_{el} and homogeneous homonuclear electron exchange rate constant k_h. Following the assumption that the free energy of activation of the homogeneous reaction is double the free energy of activation of the electrode reaction, he obtained

$$(k_s/Z_s)^{1/2} = (k_{el}/Z_{el}) \quad \text{or} \quad k_{el}^2/k_s = Z_{el}/Z_s = \text{Constant} \qquad (3)$$

This relation, known as "Marcus Cross relation", can be written in a form, $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$ where K_{12} is the equilibrium constant for the electron transfer reaction, k_{12} is the rate constant for the cross reaction, $k_{11}$and k_{22} are the self exchange constants of the couple. The advantage of cross relation is that, in contrast to the calculation of the rates which requires data on equilibrium bond lengths and force constants (as well as the work required to form the precursor and successor complexes), the only information required to calculate the electron-transfer rate constant is the self-exchange rates of the two couples and the equilibrium constant for reaction. This has greatly facilitated the testing of various aspects of the model. The cross-relation is widely used for interpreting electron-transfer rates in both homogeneous and heterogeneous (electrochemical) systems and is finding application in a variety of other reactions, including excited state processes, atom and proton transfers, group transfers, hydride transfers and gas-phase ion-molecule reactions.

The Marcus treatment also predicts a transfer coefficient of 0.5 for heterogeneous outer sphere electron transfer at relatively low and moderate overpotentials, with deviations from this value at high overpotentials.

The various assumptions involved in Marcus treatment impose significant limitations. The estimation of inner sphere contributions by Marcus in the classical limit, considering only symmetric breathing modes is probably a substantial over simplification. However, efforts by several authors[13,14] to consider the inner sphere quantum mechanically have met with only limited success. Particularly questionable is the separation of the reorganizational contributions into inner and outer solvation values, with one handled in terms of discrete vibrational states and the other with dielectric continuum theory. Sacher and Laidler[15,16] have avoided this rather arbitrary division of the inner-outer solvation contributions by considering changes in the total sovation energy as the radius of the inner coordination sphere changes, but this approach involves continnum concepts.

The collision number in the Marcus treatment of both the homogeneous and heterogeneous electron transfer has been estimated rather crudely[17].

The assumption of negligible resonance stabilization in the activated state limits the Marcus treatment to redox systems in which the interaction between the reacting ions and electrode is weak. The Marcus treatment is more appropriate for outer sphere electron transfer electrode reactions in which the reacting central ion is separated from the electrode surface by its own inner coordination sphere as well as by a layer of adsorbed solvent molecules on the electrode surface.

An important prediction of the Marcus theory in the case of homogeneous electron transfer reaction is that electron transfer rate constants should decrease with absolute value of free energy change of the electron transfer step, i.e. both in the endothermic and exothermic regions in a series of reactions of constant reorganization energy[6-8,18-21]. . This prediction was orginally greeted with considerable scepticism. Fortunately experimentalists could report striking confirmation of this prediction[22]. Much work has been devoted to finding cases where one can observe the descending part of the Marcus curve in the exothermic region which is known as *Marcus inverted region* or simply *inverted region.* Explanations have been advanced[23,24] to explain why it has been difficult or even impossible to find examples of such behaviour for intermolecular electron transfer reactions in fluid media. Another manifestation of the inverted region is the energy gap law of radiationless transition theory. In his extension [20,25,26,27] Marcus has considered the effect of nuclear tunneling corrections and has shown those to be small for any cases of interest. Other extensions include the effect of separation distance and the mutual orientations of the redox sites on electron-transfer rates and application to biological systems. The redox centers in biological systems are frequently far apart. As a consequence the electronic transmission factors are generally less than unity i.e. the reactions are electronically non-adiabatic and the magnitude of the transmission factors are sensitive to the distance and orientation of the two redox sites. For further details of contributions of Marcus to electron transfer theory, see reference 28.

Marcus has taken the dynamical effect of solvent on electron transfer rates in many of his recent papers. Marcus and Sumi[29] showed that the intramolecular vibrational effect can modify the effect of solvent dynamics on the electron transfer rate. Marcus and Nadler[30], have derived a reaction diffusion equation for the description of the electron transfer reaction in a solution, which takes into account of both solvent and intramolecular vibrational contributions.

Recently, Marcus[31-33] has extended his theory to the electron transfer reaction between a reactant in one liquid and a second reactant in a second immiscible liquid, across an sharp interfacial boundry. Actually this is an extension of "Marcus Cross relation" earlier he derived for one phase electron transfer reaction (equation 3).

(1.b) Hush's Approach

Marcus has assumed negligible resonance stabilization in the activated state so that his approach was limited to redox systems in which there is weak interaction between the reacting ions and electrode. In contrast, Hush[4] has assumed that the resonance stabilization is sufficient for the transferred electron to become delocalised and distributed between the reacting ions in the homogeneous case or between the reacting ions and the electrode in the heterogeneous case.

(1.c) The Levich, Dogonadze and Kuznetsov (LDK) Approach

In their initial publications[5,34], Levich, Dogonadze and Kuznetsov considered the reacting ion with its inner coordination sphere as a frozen system, which does not contribute in any way to the activation process. The potential energy of the electron in this frozen system, however, depends on the polarization of the solvent near the ion. Since the molecules of the solvent are in continuous thermal movement, the polarization of the solvent surrounding the ion fluctuates with time until a state of polarization is reached where a radiationless electron transfer can take place between the ion and electrode by tunneling. After the electron transfer, the polarization of the solvent surrounding the ion is the same as the polarization prior to the transfer and then decays as the system reverts to the equilibrium polarization of the final state. The transition probability of the system from the initial state to the final state is calculated using first order perturbation theory, assuming the Frank-Condon principle to apply to this system and using the Born-Oppenheimer approximation. The authors also calculate the transition probability in different temperature limits[35].

The LDK treatment considers the solvent to be dielectric continuum and they do not include any contribution from the inner solvent sphere. Schmickler and Vielstich[47], Kestner *et al*[14] have pointed out the importance of taking such effects into account.

Kuznetsov[36] has proposed a generalised model for electrochemical charge transfer reaction in the adiabatic limit. All the former models for the process considered only the change of the solvent polarization as the reaction co-ordinate whereas the author in his new model[36] had emphasized the significance of the motion of reacting ion and described the new model in terms of two reaction co-ordinates - change of solvent polarization as well as the motion of reacting ion.

Kuznetsov *et al*[37] put forward a theoretical model to describe the effects of ionic atmosphere of the ion on the dynamics of the electron transfer process. He found that the ionic atmosphere will effect the electrostatic part of the free energy of activation. He[38] used a variational principle to estimate the rates of a non-adiabatic charge transfer reaction occuring in a polar liquid. He[39] also developed a two-mode configuration model to describe a adiabatic electron transfer process between a donor and an acceptor molecule. The motion was found to be stochastic and overdamped and a Langevin equation was used to describe the motion.

Kuznetsov has reviewed[40] the different theoretical treatments for the effects of medium polarization on the dynamics of charge transfer reactions occuring in adiabatic and diabatic limits. He[41] has extended the theory to electron transfer at a superconducting electrode.

The energetics of thermal and optical electron exchange reactions was studied by Kuznetsov *et al*[42] using extended Debye-Huckel model, taking Ferrocenium-Ferrocene system as an example. They found that the activation free energy associated with the reorganization of the ionic atmosphere for the two processes increases with increasing internuclear distance between the ractants as a result of diminished sharing of the ionic cloud surrounding the donor and acceptor molecules.

Kuznetsov[43] has extended the solvent polarization model to describe an adiabatic SN_2 substitution reaction proceding in a polar solvent. The expression for the transition probabilty have been derived in the slow and fast relaxation regimes and he showed that Frank-Condon barrier for the transition is created by the solvent polarization.

The activation energy for the charge transfer process in solution is usually given by reorganization of the solvent following the process. Kuznetsov and German[44] have given a brief account of the recent methods and models for calculating the reorgnization energy. They have also discussed the experimental data of structural and optical properties of the metal complexes in relation to the charge transfer process and the method of calculating the inner sphere reorganization energy resulting from the change of oxidation state of the central metal atom.

Kuznetsov and Izotov[45] have discussed the important effect of electrode potential on the reorganization energy of the solvent for the charge transfer process taking H_2O/Mg system as an example. The authors[46] also considered the effect of electrode potential on the image forces of the point charges near an electrode-electrolyte interface, describing the solvent as dielectric continuum and calculations were carried out using linear response theory.

(2) OTHER TREATMENTS

Schmickler and Vielstich[13,47], Kestner, Logan and Jortner[14] and Schmidt[48-50] have examined the theory of outer sphere electron transfer reactions, using essentially the LDK model. Different formalisms have been attempted and improvements in the orginal model have been made.

(3) COMPARISON OF THEORY AND EXPERIMENT

Hale[51] has made a comparison between theoretical and experimental values of free energy of activation for outer sphere electron transfer reactions using Marcus treatment and showed that there is good agreement between these two.

(4) ELECTROCHEMICAL PROTON TRANSFER REACTION - DIFFERENT APPROACHES

The various treatments include different models for activations. Until 1967, the process of activation for electrochemical proton transfer event to take place was thought of in terms of a model[52] om which OH bond stretching in the H_3O^+ ion leads to transfer of the proton to an adsorbed state on the metal electrode surface, coupled with transfer of an electron and dehydration of proton. Later treatments recognise that some reorganised state of the hydrated proton must arise by classical thermal activation and to this state an electron is transferred in a radiationless transition producing H- interacting both with the metal surface and with neighbouring H_2O molecules. The system then relaxes to the lowest energy state at temperature T of H adsorbed at the metal and of water molecules nearby, in the interface.

In 1967, another approach[53] was considered, in which the hydration shell of H_3O^+ becoming thermally activated and not the OH bond itself in H_3O^+. Proton transfer then occurs by a non-classical quantum-mechanical tunneling step from H_3O^+ in its thermally activated hydration envelope to a state on the surface.

Pioneering theoretical contribution towards the electrochemical proton transfer reaction was made by Gurney[54]. Following his treatment another important model, activated complex model, was put forward by Bockris and Matthews[60,61].

(4.a) Activated Complex Approach

Since pioneering work of Horiuti & Polanyi[55], various authors[52,56-59] have used the activated complex approach involving the stretching of OH bond in H_3O^+ to form transition state of the form O-H-metal. Bockris and Matthews[60,61] have proposed a model, in which the initial state of the system is a solvated H_3O^+ ion at the outer Helmboltz plane (Fig .II). One of the protons associated with H_3O^+ ion then transfers to one of the solvation water molecules situated at a distance δ_r, estimated by Bockris and Matthews[60] to be 3.8 A°. Further transfer of a proton to a water molecule immediately adjacent to the surface is not considered because these authors believe that the strong negative charge of the electrode surface preferentially orients the water molecules on the electrode surface and further transfer of the proton to the surface water causes the break down of normal water structure at the electrode surface.

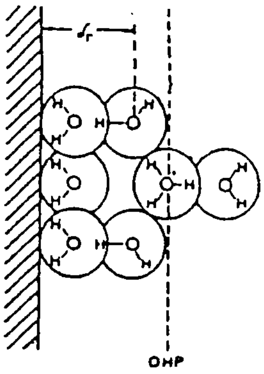

Fig.II. Bockris-Matthews model for the electrode interface in proton discharge from H_3O^+.

Bockris and Matthews[60,61] consider the electron to be transferred by tunneling in the activated state because the barrier height is otherwise too high for classical transfer.

The authors[60] also considered the probability of proton tunneling through the barrier, as an alternative to proton transmission over the barrier. They have examined the problem of proton tunneling using various potential energy barriers.

(4.b) The Non-Equilibrium solvent Polarization model (Solvent Reorganization model)

The first quantum-mechanical model of a proton transfer taking into account the dynamical role of the solvent polarization was suggested in 1967, by Dogonadze, Kuznetsov and Levich[53,62]. According to this model, the discharge of H_3O^+ ion located at some fixed distance occurs in the following way[53]. In the initial state the proton vibrates in the H_3O^+ ion in various vibrational states according to the thermal distribution. In the initial equilibrium configuration of the medium molecules, the vibrational energy levels of the proton are not equal to those for the proton in the adsorbed state at the electrode. A classical fluctuation of the molecular surroundings lead to matching of a given pair of proton energy levels. In this configuration, a quantum, sub-barrier, proton transition from the vibrational level in H_3O^+ ion to a corresponding vibrational level of the adsorbed state occurs. A change in the state of the electrons in the metal takes place when the proton goes under the barrier in the region of values of its co-ordinate near the point of intersection of the potential energy curves for the proton in the initial (proton in the H_3O^+ ion) and final (adsorbed hydrogen atom) states. This change in the electron state results in a redistribution of electron density and formation of a chemical bond between the proton and the metal.

With respect to the electrochemical reaction of hydrogen ions where the transfer of two particles, electron and proton occurs, the problem of whether electron transfer and the process of breaking or formation of the chemical bond are simultaneous or sequential, was discussed by Kuznetsov[63]. He arrived at the conclusion that the electron transfer and rearrangement of the chemical bond may be unified step. The character of the process depends on the potential energy surface of the system after the change of electron state. He treats the proton as well as electron as part of a fast subsystem with solvent being the slow system. The model assumes the activation can arise only due to non-equilibrium solvent polarization. By using a double adiabatic approximation, this approach separates the electron and proton wave function from the solvent wave functions and treat the electron and proton as a quantum sub system and the solvent as a classical subsystem. Then he calculates the proton transition probability using first order perturbation theory.

Within the framework of this approach German *et al*[64] have estimated the potential dependence of the isotopic separation factor. They concluded that the proton and deuterium approach distances to the electrodes are different as well potential dependent and this causes the potential dependence of separation factor. Although this approach has not been developed to the extent where a quantitative comparison with the experimental results can be carried out, the shape of the separation factor - potential curve obtained from this approach is analogous to the one experimentally observed.

Further development of basic LDK model and the detailed analysis of the dependance of the symmetry factor on the potential and temperature[66], have shown that there are additional factors which can affect the elementary act of this reaction. These investigations led to the formulation of a new model for electrochemical proton discharge i.e. charge-variation model of (CVM)[65].

(4.c) Charge-Variation Model (CVM)

In the basic model, it was assumed that the hydrogen atom in the adsorbed state is neutral and weakly influences the state of the medium molecules. This model (CVM)[65] takes into account the variation of the charge of adsorbed hydrogen in the activation-deactivation process. A model for proton transfer in weakly polar solvents was suggested recently[67].

The importance of the double layer towards the proton discharge has been considered, for the first time, through ψ_1 potential, by Frumkin[68]. Krishtalik[69] tries to explain the experimental observations in the electrochemical hydrogen evolution reaction in terms of effect of ψ_1.

A comparison of two models for electrochemical proton transfer reactions, i.e. the bond-stretching model and medium-reorganisation model, was made by Krishtalik[70], with respect to the experimental data. All the experimentally observed relationship are at variance with the conclusion of the bond stretching model and in full agreement with the prediction of the medium reorganisation model. Finally Krishtalik summarizes the results of the experimental studies on the mechanism of proton discharge as (i) the barrier for proton tunneling is not directly related to the activation energy and proton co-ordinate is not the only reaction co-ordinate and (ii) reorganization of the medium exerts a significant influence on the activation energy.

So a unified treatment, which takes into account of both contributions, bond stretching and medium reorganization, becomes necessary to treat the problem of electrochemical proton transfer reaction.

(5) TEMPERATURE DEPENDENCE OF THE SYMMETRY FACTOR, β FOR THE HER

For a variety of electrode reactions, the symmetry factor, β, that expresses the dependence of the electrochemical Gibbs energy of activation, $\Delta G^{\ddagger}_{V}$, on potential, V, viz. $\Delta G^{\ddagger}_{V} = \Delta G^{\ddagger}_{V=0} \pm \beta VF$, was taken to be independent of temperature T and a constant value of $\simeq$ 0.5. But recent experiments on electrochemical HER[71-80] showed that it is not a constant, but rather have a temperature dependence as $\beta = \beta_H + T\beta_S$, where β_H and β_S are the enthalpic and entropic components of symmetry factor, respectively.

Various theoretical explanations for this experimental observation have been given. Attempts by Kuznetsov[66] and by Ulstrup[81] to provide theoretical basis for the temperature dependence of β have resulted only in rather negative findings, viz. that only a small effect is predictable, based either on transition from nuclear tunneling to classical proton transfer with increasing temperature T or on dielectric polarization behaviour.

An explanation given by Yeager[82] was the possible role of potential in changing the extent of electron "spill-over"[83,84] in the double layer. This effect could influence solvent orientation in the double layer or is equivalent to a change of thickness[79] of the inner double-layer charge distribution, but it is unclear if there would be any significant temperature dependence of the spill-over effect involving metal electron.

Recently, Bockris and Gochev[85] have investigated theoretically, several possibilities for explanation of variation of β with temperature including the change of effective double layer thickness with temperature but no consideration was given to the solvent dipole orientation which could be an important reason for this dependence.

Schmickler[86] has taken into account the effect of electric field at the metal surface on the potential energy surface of the initial state (H_3O^+ + Metal(e^-)) and has given a theoretical explanation for the temperature dependence of β, using LDK model for the proton transfer reaction.

(6) THE REORGANISATION ENERGY OF MEDIUM DURING PROTON DISCHARGE REACTIONS

The reorganisation energy, λ, measures the work expended in the organisation of atoms and molecules in the environment of the reactant from their positions at equilibrium to the position occupied about the product species when it is at equilibrium.

In their derivations of formulae for λ, Hush[4,87] and Marcus[6-10] treated seperately, the behaviour of dielectric surrounding the reactant and that of the molecule or coordinated ion within the `charged spheres '. This enables a microscopic treatment to be made of changes of bond lengths and angles within the molecule and microscopic electrostatic treatment of the unsaturated dielectric outside the sphere. These separate contributions are represented as inner sphere and outer sphere reorganization energies respectively. In the charge transfer reactions in the solutions, the estimation of the reorganisation energy, of the medium during the reaction is very important, for the calculation of the activation barrier of the reaction, exchange current densities of one electron reactions at metal etc[51,88]. There are experimental reports of values of λ for many aquo and other complex ion systems[89] from studies of the kinetics of one-electron outer sphere redox reactions. Reorganisation energies have also been derived from exchange current densities[51] by means of theory due to Marcus. Furthermore there have been many theoretical estimates of reorganisation energies of ion based on the dielectric continuum theory with inner sphere activation[88] taken into account. However there has been little report on the magnitude of the reorganisation energy for discharge of the aqueous proton. Krishtalik[90] using the dielectric continuum theory, has estimated a value of about 1.0eV. This result may be too low because of the neglect of contribution from inner coordination sphere of water molecules. In this calculation, he has considered the hydronium ion with larger radius and so with smaller λ value. Bockris and Khan[91] have stressed the importance of inner sphere contributions. A description of the proton discharge reaction emphasizing inner-solvation sphere bond breaking and metal-hydrogen bond forming is presented in the works of Bockris and co-workers[91,92].

Recently, Frese Jr[93] has determined the reorganisation energy of aqueous proton by analysis of experimental values of exchange current densities for the proton discharge reactions of various metals. For all these systems he got a constant value of 2.0 eV indicating a constant value for the electrolyte contribution of the activation Gibbs energy for proton discharge. This reported value for reorganisation energy of 2eV is in agreement with the value given by Levich *et al*[94].

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CHAPTER III

DYNAMICS OF ELECTRON TRANSFER REACTIONS AT METAL ELECTRODES

(1) INTRODUCTION

In the preceding chapters we have given the different theoretical approaches of electrochemical electron transfer reactions. In this chapter we investigate the dynamics of an electrochemical electron transfer reaction, in the adiabatic limit. We make use of a path integral approach to the problem. In the adiabatic limit, the dynamics is governed by the instantaneous value of the energy of the acceptor orbital. Due to the coupling with the solvent, this energy is changed, by an amount that we refer to as the shift and denote by $Q(t)$. The problem then reduces to analysis of the time dependence of $Q(t)$.

Recently, Schmickler[1] has suggested an approach to adiabatic electron transfer reaction at metal electrodes. His treatment is similar to that of the Levich and Dogonodze[2] theory for non-adiabatic reactions. However the rate is not calculated perturbatively. He uses an earlier model of Schmickler[3] and Kornyshev and Schmickler[4], suggested for the study of the statics of electrochemisorption for the description of the dynamics of the electron transfer.

Schmickler's Hamiltonian is an extension of the Newns-Anderson[5,6] Hamiltonian to the electrochemical context. It has the continuum of one electron state of the metal coupled to an ionic orbital, which in turn is coupled to the solvent, the solvent being represented as a collection of harmonic oscillators. The harmonic oscillators are treated classically. The sum of the electronic energy and potential energy of the harmonic oscillators is looked at and for certain values of the parameters, it is a double well type. Schmickler[1] calculates the height of the barrier to be overcome in going from one minimum to the other and writes the rate as A exp(-barrier height/kT). An explicit expression for the barrier height is obtained in terms of the parameters occuring in the Hamiltonian. The pre-exponential factor, A, is not derived explicitly, but plausible forms for it are suggested.

Our aim is to look at the dynamics that this Hamiltonian leads to. We treat the harmonic oscillators quantum mechanically also and derive the classical result therefrom as an approximation. The Hamiltonian is very interesting in itself as one can easily integrate out the harmonic oscillator part and arrive at a description of the dynamics of the variable $Q(t)$, which is the only variable of importance in electron transfer. Within certain approximations, we show that this variable obeys a stochastic integral equation. In certain cases, this equation can be solved by converting it into a stochastic differential equation. The rate of electron transfer can be obtained from this. Thus, we obtain an exiplicit expression for Schmickler's pre-exponential factor A. The expression contains certain correction factors to the one suggested by Schmickler (see our eqn.53)

(2) THE HAMILTONIAN

The Hamiltonian of Schmickler and Kornyshev[1] and Schmickler[4] is,

$$H = \varepsilon_a n_a + \sum_k \varepsilon_k n_k + \sum_k (V_{ak} C_a^+ C_k + V_{ka} C_k^+ C_a) + n_a (\sum_\upsilon G_\upsilon q_\upsilon)$$

$$+ \sum_\upsilon (p_\upsilon^2 / 2m_\upsilon + 1/2 \, m_\upsilon \omega_\upsilon^2 q_\upsilon^2) \; . \qquad (1)$$

We have not included spin in the description at all. The neglect of spin means that each orbital can take up only one electron. The solid is described in a one electron model and ε_k are the energies of the one electron states, which have associated with them the creation and annihilation operators C_k^+ and C_k. ε_a represents the energy of the orbital on the ion, which can take up one electron, and C_a and C_a^+ are the associated annihilation and creation operators. V_{ak} and V_{ka} are the hopping matrix elements, causing the electron transfer. As will become obvious later, the restriction to a spin-less Hamiltonian and the neglect of electron-electron interactions are assumptions that can be removed easily in the adiabatic limit. The solvent is represented as a collection of harmonic oscillators, the υth harmonic oscillator having position q_υ, mass m_υ, momentum p_υ and frequency ω_υ. Notice that Schmickler writes the interaction between the electron and harmonic oscillators as $(Z-n_a)\sum_\upsilon \hbar\omega_\upsilon g_\upsilon q_\upsilon$ and that his definition of p_υ and q_υ are different from ours. As the term involving Z can be easily got rid of by a redefinition of the co-ordinates of the harmonic oscillators, we do not include Z in the Hamiltonian in equation (1). The physics of our Hamiltonian, of course, is completely equivalent to that of Schmickler's.

In the followling, it is convenient to define an electronic Hamiltonian, $H_e(Q)$ as a function of a variable Q, by

$$H_e(Q) = (\varepsilon_a+Q)n_a + \sum_k \varepsilon_k n_k + \sum_k (V_{ak}C_a^+C_k+V_{ka}C_k^+C_a). \qquad (2)$$

Hence our Hmiltonian of eqn.(1) may be written as

$$H = H_e(Q = \sum_\upsilon G_\upsilon q_\upsilon) + H_{os} \qquad (3)$$

where

$$H_{os} = \sum_\upsilon \left(p_\upsilon^2 /2m_\upsilon + 1/2\ m_\upsilon\omega_\upsilon^2 q_\upsilon{}^2 \right). \qquad (4)$$

(3) STATICS OF THE ELECTRONIC SYSTEM

For any value of Q, it is a simple problem to solve for the ground state of the Hamiltonian $H_e(Q)^{5,6}$. We shall quote the relevant results here. The important quantity is

$$\Delta(\omega) = \pi \sum_k |V_{ak}|^2 \, \delta(\omega - \varepsilon_k) \tag{5}$$

in terms of which the density of states on the ionic orbital, $\rho_a(\omega)$ can be found. We shall indicate the dependence of $\rho_a(\omega)$ on Q by writing it as $\rho_a(\omega,Q)$. It is defined by

$$\rho_a(\omega,Q) = \sum_m |\langle a|m\rangle|^2 \, \delta(\omega - \varepsilon_m) \tag{6}$$

where $|m\rangle$ stands for one electron eigen functions of $H_e(Q)$ having energy ε_m. $\rho_a(\omega,Q)$ can be written as

$$\rho_a(\omega,Q) = -1/\pi \ \mathrm{Im} \ \langle a|(\omega + io - H_e(Q))^{-1}|a\rangle \ . \tag{7}$$

Assuming the metal band to extend from $-\infty$ to ∞ and $\Delta(\omega)$ to be independent of ω (the wide band approximation), one can obtain^{5,6}

$$\rho_a(\omega,Q) = \frac{\Delta}{\pi \left((\omega - \varepsilon_a - Q)^2 + \Delta^2 \right)} \ . \tag{8}$$

The occupation number of the ionic orbital, if the system is in its ground state, is

$$\langle n_a \rangle = \int_{-\infty}^{\varepsilon_F} d\omega \, \rho_a(\omega,Q) \tag{9}$$

$$= 1/\pi \tan^{-1}((\varepsilon_F - \varepsilon_a - Q)/\Delta) + 1/2 \quad (10)$$

where ε_F denotes the Fermi level of the metal. The brackets in $\langle n_a \rangle$ indicate taking expectation values with respect to the ground state. We shall also make use of the following results of the application of the Hellmann-Feynman theorem to the Hamiltonian $H_e(Q)$. If E(Q) denotes ground state energy of $H_e(Q)$ then

$$\partial E(Q)/\partial Q = \langle \partial H_e(Q)/\partial Q \rangle = \langle n_a \rangle \quad (11)$$

the last step following easily from the definition of $H_e(Q)$ in equation (2).

(4) DYNAMICS OF ELECTRON TRANSFER

(4.a) The Shift and its dynamics

We are interested in the adiabatic limit of the electron transfer reaction. This means that the width of the ionic orbital has to be much larger than the quantum $\hbar\omega_m$, of the harmonic oscillator of highest frequency. In this limit $\hbar\omega_m/\Delta \ll 1$ and then the electronic system adjusts instantaneously to the positions of the harmonic oscillators. Looking at the coupling term between the oscillators and the electrons in the Hamiltonian in equation (1), we realise that it may be combined with the term $\varepsilon_a n_a$ and written as $(\varepsilon_a + \sum_\upsilon q_\upsilon G_\upsilon) n_a$. This means the effective energy of this orbital is shifted because of the interaction with the harmonic oscillators. So, we introduce the shift of the ionic orbital at time t by $Q(t) = \sum_{\upsilon} G_{\upsilon} q_{\upsilon}(t)$.

The fact that the electron transfer is adiabatic implies that one is interested only in the instantaneous value of the shift Q(t), since a knowledge of this would enable us to calculate the electronic structure. Thus, the shift is our reaction co-ordinate and the problem reduces essentially to a study of its dynamics. We make use of path integral techniques to do this. To understand our approach, consider a system which needs only one co-ordinate to specify it, which we denote by q. If the system is known to be at q_i at the time t_i then the probability of finding it at the time t_f at the position q_f is given by

$$P(q_f, t_f | q_i, t_i) = \left| \int_{q(t_i)=q_i}^{q(t_f)=q_f} Dq(t) \exp\{i/\hbar\, S[q]\} \right|^2$$

$$= \int_{q(t_i)=q_i=\tilde{q}(t_i)}^{q(t_f)=q_f=\tilde{q}(t_f)} Dq(t) \int D\tilde{q}(t) \exp\left[\frac{i}{\hbar}(S[q]-S[\tilde{q}])\right]. \tag{12}$$

The path integration in equation (12) are over all paths q(t) and $\tilde{q}(t)$ obeying $q(t_i) = \tilde{q}(t_i) = q_i$ and $q(t_f) = \tilde{q}(t_f) = q_f$. S[q] is the action, which is a functional of the path q(t) (we indicate functional dependences with square brackets). In a similar fashion, for the electron transfer problem, we wish to calculate the probability that $Q(t)$ will have a value Q_f at the time t_f given that it had a value Q_i at the time t_i. Our aim is to write this probability, $P(Q_f, t_f | Q_i, t_i)$ as a double path integral over paths of the shift variable, as is done in equation (12).

As the system is at a temperature T, and as the shift is taken to have a value Q_i, we represent the state of the system at the time t_i by the density operator[7]

$$\rho(t_i, \underline{q}_i, \underline{\tilde{q}}_i) = N_0\, e^{-\beta H_e(Q)} \left(\rho_{os}(\underline{q}_i, \underline{\tilde{q}}_i) \right)_{\sum_\upsilon G_\upsilon q_{\upsilon i} = \sum_\upsilon G_\upsilon \tilde{q}_{\upsilon i} = Q_i} \tag{13}$$

with $\beta = 1/kT$. In the above, we have used a mixed representation. Thus the density operator for the electronic system is written as an operator itself, while for the harmonic oscillator part, we have written the matrix element of the operator, so that the condition that the shift has a value Q_i can be easily imposed. $\rho(t_i, \underline{q}_i, \underline{\tilde{q}}_i)$ is better referred to as a density operator-matrix, but we shall simply refer to it as density operator. In equation (13)

$$\rho_{os}(\underline{q}_i, \underline{\tilde{q}}_i) = \langle \underline{q}_i | e^{-\beta H_{os}} | \underline{\tilde{q}}_i \rangle \tag{14}$$

where q_i stand for the positions $q_{i1}, q_{i2}, \ldots, q_{i\upsilon}, \ldots$ of the harmonic oscillators and $|\underline{q}_i>$ is the associated eigen vector. N_o is a normalisation factor, which guarantees normalisation of the density operator.

In order to calculate the probability $P(Q_f, t_f | Q_i, t_i)$, we have to evolve $\rho(t_{\underline{i}}, q_{\underline{f}}, \tilde{q}_f)$ from t_i to t_f. This gives

$$\rho(t_f, \underline{q}_f, \tilde{\underline{q}}_f) = N_o \int d\underline{q}_i \int d\tilde{\underline{q}}_i \int_{\underline{q}(t_i)=\underline{q}_i}^{\underline{q}(t_f)=\underline{q}_f} D\underline{q}(t) \int_{\tilde{\underline{q}}(t_i)=\tilde{\underline{q}}_i}^{\tilde{\underline{q}}(t_f)=\tilde{\underline{q}}_f} D\tilde{\underline{q}}(t)$$

$$\times \exp i/\hbar \{S_{os}[\underline{q}\ ]-S_{os}[\tilde{\underline{q}}\ ]\} \rho_{os}(\underline{q}_i, \tilde{\underline{q}}_i)\ \delta(Q_i - \sum_\upsilon G_\upsilon q_{\upsilon i}) \delta(Q_i - \sum_\upsilon G_\upsilon \tilde{q}_{\upsilon i})$$

$$\times U_e(t_f, t_i; [\underline{q}(t)]\ e^{-\beta H_e(Q_i)}\ U_e(t_f, t_i; [\tilde{\underline{q}}(t)]) \qquad (15)$$

where $d\underline{q}_i = \prod_\upsilon dq_{\upsilon i}$ and $d\tilde{\underline{q}}_i = \prod_\upsilon dq_{\upsilon i}$. $S_{os}[\underline{q}]$ is total action for the harmonic oscillators, given by

$$S_{os}[\underline{q}\ ] = \sum_\upsilon \int_{t_i}^{t_f} dt \frac{m_\upsilon}{2} (\dot{q}_\upsilon^{\,2} - \omega_\upsilon^{\,2}\, q_\upsilon^{\,2}\ )$$

$\dot{q}_\upsilon = dq_\upsilon/dt$. $\underline{q}(t)$ and $\tilde{\underline{q}}(t)$ are paths for the harmonic oscillators that start at $\underline{q}_i$ and $\tilde{\underline{q}}_i$, respectively, at the time t_i and end at $\underline{q}_f$ and $\tilde{\underline{q}}_f$ at the time t_f. $U_e(t_f, t_i; [q(t)])$ is the time development operator for the electronic part, which is under the influence of harmonic oscillators, following the trajectory q(t) (see Pechukas[8] for this type of describing the time development of a system). The required probability is

$$P(Q_f,\ t_f | Q_i,\ t_i) =$$

$$\int d\underline{q}_f \int d\tilde{\underline{q}}_f\ \delta(\underline{q}_f-\tilde{\underline{q}}_f)\ \delta(Q_f-\sum_{\nu} G_{\nu} q_{\nu f})\ \mathrm{Tr}_e\{\rho(t_f,\ \underline{q}_f,\ \tilde{\underline{q}}_f)\ . \tag{16}$$

Tr_e denotes a trace operation over the electronic part. The above may be written in more detail as

$$P(Q_f,\ t_f | Q_i,\ t_i) = N_o \int d\underline{q}_f \int d\tilde{\underline{q}}_f\ \delta(\underline{q}_f-\tilde{\underline{q}}_f)\ \delta(Q_f-\sum_{\nu} G_{\nu} q_{\nu f}) \int d\underline{q}_i \int d\tilde{\underline{q}}_i$$

$$\times\ \delta(Q_i-\sum_{\nu} G_{\nu} q_{\nu i})\ \delta(Q_i-\sum_{\nu} G_i \tilde{q}_{\nu i})\ \rho_{os}(\underline{q}_i, \tilde{\underline{q}}_i) \int_{\underline{q}(t_i)=\underline{q}_i}^{\underline{q}(t_f)=\underline{q}_f} D\underline{q}(t) \int_{\tilde{\underline{q}}(t_i)=\tilde{\underline{q}}_i}^{\tilde{\underline{q}}(t_f)=\tilde{\underline{q}}_f} D\tilde{\underline{q}}(t)$$

$$\times\ \exp i/\hbar\ \{S_{os}[\underline{q}]-S_{os}[\tilde{\underline{q}}\ ]\}\ \mathrm{Tr}_e\{U_e(t_f,\ t_i;\ [\underline{q}(t)])\qquad e^{-\beta H_e(Q_i)}$$

$$\times\ U_e^{+}\ (t_f,\ t_i;\ [\underline{q}(t)])\}\ . \tag{17}$$

We now introduce two continuous functions $Q(t)$ and $\tilde{Q}(t)$ with $t_i \leq t \leq t_f$. Also we divide the time interval $(t_i,\ t_f)$ into N subintervals, each of length Δt such that $N\ \Delta t = t_f - t_i$.

We may write

$$1 = \lim_{N \longrightarrow \infty} \int \cdots\cdots \int \prod_{\alpha=1}^{N-1} \{dQ(t_\alpha)\, d\tilde{Q}(t_\alpha)\, \delta(Q(t_\alpha) - \sum_\upsilon G_\upsilon q_\upsilon(t_\alpha))$$

$$\times\, \delta(\tilde{Q}(t_\alpha) - \sum_\upsilon G_\upsilon \tilde{q}_\upsilon(t_\alpha))\} \tag{18}$$

where $t_\alpha = t_i + \alpha\Delta t$, $\alpha = 1,2,3,\ldots\ldots, N-1$.

So $P(Q_f, t_f | Q_i, t_i)$ may be written as

$$P(Q_f, t_f | Q_i, t_i)$$

$$= \lim_{N \longrightarrow \infty} \int d\underline{q}_f \int d\underline{\tilde{q}}_f\, \delta(\underline{q}_f - \underline{\tilde{q}}_f)\, \delta(Q_f - \sum_\upsilon G_\upsilon q_{\upsilon f}) \int d\underline{q}_i \int d\underline{\tilde{q}}_i$$

$$\times\, \delta(Q_i - \sum_\upsilon G_\upsilon q_{\upsilon i})\, \delta(Q_i - \sum_\upsilon G_\upsilon \tilde{q}_{\upsilon i}) \int_{\underline{q}(t_i)=\underline{q}_i}^{\underline{q}(t_f)=\underline{q}_f} D\underline{q}(t) \int_{\underline{\tilde{q}}(t_i)=\underline{\tilde{q}}_i}^{\underline{\tilde{q}}(t_f)=\underline{\tilde{q}}_f} D\underline{\tilde{q}}(t)$$

$$\times\, \exp i/\hbar\, \{S_{os}[\underline{q}\ ] - S_{os}[\underline{\tilde{q}}\ ]\}\, \rho_{os}[\underline{q}_i, \underline{\tilde{q}}_i]\, Tr_e\{U_e(t_f, t_i; [\underline{q}(t)])$$

$$\times\, e^{-\beta H_e(Q_i)}\, U_e^{+}(t_f, t_i; [\underline{\tilde{q}}(t)])\} \prod_{\alpha=1}^{N-1} \int dQ(t_\alpha) \int d\tilde{Q}(t_\alpha)\, \delta(Q(t_\alpha) - \sum_\upsilon G_\upsilon q_\upsilon(t_\alpha))$$

$$\times\, \delta(\tilde{Q}(t_\alpha) - \sum_\upsilon G_\upsilon \tilde{q}_\upsilon(t_\alpha))\ . \tag{19}$$

The time development operator $U_e(t_i, t_f; [\underline{q}(t)])$ depends only on $\sum_\upsilon G_\upsilon q_\upsilon(t)$ which because of the delta functions in equation (19), is equal to $Q(t)$. So we can write the above equation as

$$P(Q_f,\ t_f | Q_i,\ t_i)$$

$$= N_0 \int d\underline{q}_f \int d\tilde{\underline{q}}_f\ \delta(\underline{q}_f, \tilde{\underline{q}}_f) \int dQ_f \int dQ_i \delta(Q_i - \tilde{Q}_i) \int d\underline{q}_i \int d\tilde{\underline{q}}_i$$

$$\times \int_{\underline{q}(t_i)=\underline{q}_i}^{\underline{q}(t_f)=\underline{q}_f} D\underline{q}(t) \int_{\tilde{\underline{q}}(t_i)=\tilde{\underline{q}}_i}^{\tilde{\underline{q}}(t_f)=\tilde{\underline{q}}_f} D\tilde{\underline{q}}(t)\ \exp i/\hbar\ \{S_{os}[\underline{q}] - S_{os}[\tilde{\underline{q}}\ ]\}$$

$$\times \lim_{N \longrightarrow \infty} \prod_{\beta=1}^{N-1} \int dQ(t_\beta) \int d\tilde{Q}\ (t_\beta) \prod_{\alpha=0}^{N} \delta(Q(t_\alpha) - \sum_{\upsilon} G_\upsilon q_\upsilon(t_\alpha))$$

$$\times \delta(\tilde{Q}(t_\alpha) - \sum_{\upsilon} G_\upsilon \tilde{q}_\upsilon(t_\alpha))\ \rho_{os}(\underline{q}_i, \tilde{\underline{q}}_i)\ \mathrm{Tr}_e\{U_e(t_f, t_i; [q(t)])\ e^{-\beta H_e(Q_i)}$$

$$\times U_e(t_f, t_i;\ [\tilde{Q}(t)])\}\ . \qquad (20)$$

In the above, we have defined $Q(t_i) = Q_i$, $\tilde{Q}(t_i) = \tilde{Q}_i$, $Q(t_f) = Q_f$ and $\tilde{Q}(t_f) = \tilde{Q}_f$.

Now the delta functions in equation (20) may be expressed in terms of Fourier integrals, i. e.,

$$\prod_{\alpha=0}^{N} \delta(Q(t_\alpha)-\sum_\nu G_\nu q_\nu(t_\alpha))\ \delta(\tilde{Q}(t_\alpha)-\sum_\nu G_\nu \tilde{q}_\nu(t_\alpha))$$

$$= \left[\frac{1}{2\pi\hbar}\right]^{N+1} \int \cdots\cdots \int \prod_{\alpha=0}^{N} dp_\alpha\ d\tilde{p}_\alpha\ \exp\left[\frac{i}{\hbar}\sum_{\alpha=0}^{N} p_\alpha\{Q(t_\alpha)\right.$$

$$\left. - \sum_\nu G_\nu q_\nu(t_\alpha)\} - \frac{i}{\hbar}\sum_{\alpha=0}^{N} \tilde{p}_\alpha\ \{\tilde{Q}(t_\alpha) - \sum_\nu G_\nu \tilde{q}_\nu(t_\alpha)\}\right] . \qquad (21)$$

Defining $t_0 = t_i+i0$, $t_N=t_f-i0$ and $P(t) = \sum_{\alpha=0}^{N} p_\alpha \delta(t-t_\alpha)$, we can write the left hand side of equation (21) as

$$\left[\frac{1}{2\pi\hbar}\right]^{2(N+1)} \int \cdots\cdots \int \prod_{\alpha=0}^{N} dp_\alpha\ d\tilde{p}_\alpha\ \exp\left[\frac{i}{\hbar}\ \{\int_{t_i}^{t_f} dt(p(t)Q(t)-p(t)\right.$$

$$\left. \times \sum_\nu G_\nu q_\nu(t) + \tilde{p}(t) \sum_\nu G_\nu \tilde{q}_\nu(t) - \tilde{p}(t)\ \tilde{Q}(t))\}\right] . \qquad (22)$$

In the limit N ——> ∞ we write this symbolically as

$$\int Dp(t) \int D\tilde{p}(t) \exp \left[\frac{i}{\hbar}\left[\int_{t_i}^{t_f} dt\left[p(t)Q(t)-\tilde{p}(t)\tilde{Q}(t)-p(t)\sum_{\upsilon}G_{\upsilon}q_{\upsilon}(t)\right.\right.\right.$$

$$\left.\left.\left. + \tilde{p}(t) \sum_{\upsilon} G_{\upsilon}\tilde{q}_{\upsilon}(t)\right] \right] \right] .$$

Adopting a similar notation for the integrations over the Qs, we get

$$P(Q_f, t_f|Q_i, t_i)$$

$$=N_0 \int d\underline{q}_f \int d\underline{\tilde{q}}_f\, \delta(\underline{q}_f-\underline{\tilde{q}}_f) \int dQ_f \int d\tilde{Q}_i\, \delta(Q_i-\tilde{Q}_i)\int d\underline{q}_i \int d\underline{\tilde{q}}_i$$

$$\times \int D\underline{q}(t) \int D\underline{\tilde{q}}(t) \int Dp(t) \int D\tilde{p}(t) \int DQ(t) \int D\tilde{Q}(t) \exp \left[\frac{i}{\hbar} \int_{t_i}^{t_f} dt\right.$$

$$\times \left[p(t)Q(t)-\tilde{p}(t)\tilde{Q}(t) \right] + \frac{i}{\hbar} \left[S_{os}[\underline{q}\ ]-S_{os}[\underline{\tilde{q}}\ ] \right] + \frac{i}{\hbar} \int_{t_i}^{t_f} dt$$

$$\times\left.\left[- \sum_{\upsilon}G_{\upsilon}q_{\upsilon}(t)p(t) + \sum_{\upsilon} G_{\upsilon}\tilde{q}_{\upsilon}(t)\ \tilde{p}(t)\right]\right] \rho_{os}(\underline{q}_i,\underline{\tilde{q}}_i)$$

$$\times \mathrm{Tr}_e\left[U_e(t_f, t_i; [Q(t)])\, e^{-\beta H_e(Q_i)}\, U_e^{+} (t_f, t_i; [\tilde{Q}(t)])\right] . \qquad (23)$$

Following the arguments in the appendix A, we obtain

$$\mathrm{Tr}_e\Big[U_e(t_f,\ t_i;\ [Q(t)])\ e^{-\beta H_e(Q_i)}\ U_e^{+}(t\ ,\ t\ ;\ [\tilde{Q}(t)])\Big]$$

$$= \exp\Big[\frac{i}{\hbar}\int_{t_i}^{t_f} dt\ \{E(\tilde{Q}(t)) - E(Q(t))\}\Big]\ \mathrm{Tr}_e\ e^{-\beta H_e(Q_i)}$$

So

$$P(Q_f,\ t_f|Q_i,\ t_i)$$

$$= N_0\int d\underline{q}_f\int d\tilde{\underline{q}}_f\ \delta(\underline{q}_f-\tilde{\underline{q}}_f)\int dQ_f\int d\tilde{Q}_i\delta(Q_i-\tilde{Q}_i)\int d\underline{q}_i\int d\tilde{\underline{q}}_i$$

$$\times\int D\underline{q}(t)\int D\tilde{\underline{q}}(t)\int DQ(t)\int D\tilde{Q}(t)\int Dp(t)\int D\tilde{p}(t)\ \exp\Big[\frac{i}{\hbar}\int_{t_i}^{t_f} dt$$

$$\times\Big[\ p(t)Q(t)-E(Q(t))-\tilde{p}(t)\tilde{Q}(t)+E(\tilde{Q}(t))+\sum_{\nu} G_{\nu}\tilde{q}_{\nu}(t)\tilde{p}(t)-\sum_{\nu} G_{\nu}q_{\nu}(t)p(t)\Big]$$

$$+\frac{i}{\hbar}\Big[\ S_{os}[\underline{q}\ ]-\ S_{os}[\tilde{\underline{q}}\ ]\ \Big]\ \Big]\ \rho_{os}(\underline{q}_i,\ \tilde{\underline{q}}_i)\ .$$

We have absorbed $\mathrm{Tr}_e e^{-\beta H_e(Q_i)}$ into the normalisation constant N_0. Changing over from path integral to operator notation, the above can be written as

$$P(Q_f,\ t_f|Q_i,\ t_i)\ =\ N_0\int dQ_f\int d\tilde{Q}_i\delta(Q_i-\tilde{Q}_i)\int DQ(t)\int D\tilde{Q}(t)\int Dp(t)$$

$$\times\int D\tilde{p}(t)\ \exp\ \frac{i}{\hbar}\int_{t_i}^{t_f} dt\ \{p(t)Q(t)-E(Q(t))-\ \tilde{p}(t)\tilde{Q}(t)+\ E(\tilde{Q}(t)\}$$

$$\times\ \mathrm{Tr}_{os}\Big[\ U_{os}(t_f,\ t_i;\ [p(t)])\ e^{-\beta H_{os}}\ U_{os}^{+}(t_f,\ t_i;\ [\tilde{p}(t)])\ \Big]$$

$U_{os}(t_f,\ t_i;\ [p(t)])$ is the time-development operator for the harmonic oscillators, when the νth oscillator is subjected to the force $-G_\upsilon p(t)$. Tr_{os} denotes trace operation over the harmonic oscillators. This can now be done exactly. The result is (see reference 9)

$$
\begin{aligned}
&P(Q_f, t_f | Q_i, t_i) \\
&\quad = N_o \int dQ_f \int d\tilde{Q}_i \delta(Q_i - \tilde{Q}_i) \int_{Q(t_i)=Q_i}^{Q(t_f)=Q_f} DQ(t) \int_{\tilde{Q}(t_i)=\tilde{Q}_i}^{\tilde{Q}(t_f)=\tilde{Q}_f} D\tilde{Q}(t) \int Dpt) \\
&\times \int D\tilde{p}(t) \exp\Big[\frac{i}{\hbar} \int_{t_i}^{t_f} dt \, \{p(t)Q(t) - E(Q(t)) - \tilde{p}(t)\tilde{Q}(t) + E(\tilde{Q}(t))\} - \frac{i}{2\hbar^2} \\
&\times \int_{t_i}^{t_f} dt \int_{t_i}^{t_f} ds \, \{p(t) - \tilde{p}(t)\} \{p(s) - \tilde{p}(s)\} R(t-s) + \frac{i}{2\hbar} \int_{t_i}^{t_f} dt \int_{t_i}^{t} ds \\
&\times \{p(t) - \tilde{p}(t)\} \{p(s) + \tilde{p}(s)\} I(t-s) \Big] .
\end{aligned}
\tag{24}
$$

In equation (24), R and I are defined by

$$
R(t) = \hbar \sum_\upsilon \frac{G_\upsilon^2}{2m_\upsilon \omega_\upsilon} \coth\left[\frac{\beta\hbar\omega_\upsilon}{2}\right] \cos(\omega_\upsilon t) \tag{25}
$$

and

$$
I(t) = \sum_\upsilon \frac{G_\upsilon^2}{m_\upsilon \omega_\upsilon} \sin(\omega_\upsilon t) . \tag{26}
$$

We now change over to a new set of variables for the path integrations in equation (24) by defining the centre of mass and relative co-ordinates by

$$P_C(t) = \frac{1}{2}\,(p(t)+\tilde{p}(t)) \qquad Q_C(t) = \frac{1}{2}\,(Q(t)+\tilde{Q}(t))$$

$$P_R(t) = p(t)-\tilde{p}(t) \qquad Q_R(t) = Q(t)-\tilde{Q}(t)\ . \tag{27}$$

Then

$$\begin{aligned} P(Q_f,\ t_f|Q_i,\ t_i) &= N_o \int dQ_R(t_f) \int dQ_R(t_i)\ \delta(Q_R(t_i)) \int_{Q_C(t_i)=Q_i}^{Q_C(t_f)=Q_f} DQ_C(t) \int DQ_R(t) \\ &\times \int DP_R(t) \int DP_C(t)\ \exp\Big[\frac{i}{\hbar} \int_{t_i}^{t_f} dt\ \Big[P_C(t)Q_R(t)+P_R(t)Q_C(t)-E\Big(\ Q_C + \frac{Q_R}{2}\ \Big) \\ &+ E\Big(\ Q_C - \frac{Q_R}{2}\ \Big) + \int P_R(t) \int_{t_i}^{t_f} ds\ I(t-s)\ P_C(s)\Big] - \frac{i}{2\hbar^2} \int_{t_i}^{t_f} dt \\ &\times \int_{t_i}^{t_f} ds\ P_R(t)\ R(t-s)\ P_C(t)\ \Big]\ . \end{aligned} \tag{28}$$

We now introduce a Gaussian, stationary random function $\beta(t)$, having mean zero and autocorrelation $R(t-s)$. For such a random function, $<\beta(t)\beta(s)>_\beta = R(t-s)$ and

$$< \exp\Big[\frac{i}{\hbar} \int_{t_i}^{t_f} dt\ \beta(t)P_R(t)\Big] >_\beta$$

$$= \exp\Big[\frac{-1}{2\hbar^2} \int_{t_i}^{t_f} dt \int_{t_i}^{t_f} ds\ P_R(t)R(t-s)P_R(s)\Big]\ . \tag{29}$$

In the above $<....>_\beta$ denotes averaging with respect to the random function $\beta(t)$. We make use of this in equation (28), to obtain

$$P(Q_f,\ t_f | Q_i,\ t_i)$$

$$= N_o \int_{Q_C(t_i)=Q_i}^{Q_C(t_f)=Q_f} DQ_C(t) \int_{Q_R(0)=0} DQ_R(t) \int DP_R(t) \int DP_C(t) < \exp \frac{i}{\hbar}$$

$$\times \int_{t_i}^{t_f} dt \Big[P_C(t)Q_R(t) + P_R(t)Q_C(t) - P_R(t)\beta(t) - E\Big(Q_C + \frac{Q_R}{2} \Big)$$

$$+ E\Big(Q_C - \frac{Q_R}{2} \Big) - P_R(t) \int_{t_i}^{t_f} ds\ I(t-s)\ P_C(s) \Big] >_\beta . \qquad (30)$$

The integration over $P_R(t)$ can now be performed, to obta

$$P(Q_f,\ t_f | Q_i,\ t_i) = N_o \int DQ_C(t) \int DP_C(t) \int_{Q(0)=0} DQ_R(t) \exp \frac{i}{\hbar}$$

$$\times \int_{t_i}^{t_f} dt \Big[P_C(t)Q_R(t) - E(Q_C(t) + Q_R(t) + E\Big(Q_C(t) - \frac{Q_R(t)}{2} \Big) \Big]$$

$$\times < \delta \Big[Q_C(t) - \beta(t) + \int_{t_i}^{t} ds\ I(t-s)\ P_C(s) \Big] >_\beta \qquad (31)$$

$\delta\ [Q_C(t) - \beta(t) + \int_{t_i}^{t} ds\ I(t-s) P_C(s)]$ is the delata functional (i. e., a product of an infinite number of Dirac delta functions). To make further progress, we expand $E(Q_C(t)+Q_R(t)/2) - E(Q_C(t)-Q_R(t)/2)$

in the exponent, as a Taylor series in $Q_R(t)$ to obtain

$$P(Q_f, t_f | Q_i, t_i) = N_o \int DQ_C(t) \int DP_C(t) \int DQ_R(t) \exp \frac{i}{\hbar} \int_{t_i}^{t_f} dt$$

$$\times \left[P_C(t) Q_R(t) - E'(Q_C(t))\, Q_R(t) - E'''(Q_C(t)) \frac{Q_R(t)^3}{24} + \ldots\ldots \right]$$

$$\times < \delta \left[Q_C(t) - \beta(t) + \int_{t_i}^{t} ds\, I(t-s)\, P_C(s) \right] >_\beta \tag{32}$$

with $E'(Q) = \frac{\partial E(Q)}{\partial Q}$, $E'''(Q) = \frac{\partial^3 E}{\partial Q^3}$, etc.

Neglecting terms involving the third and higher derivatives of E in the exponent, we can carry out the integration over $Q_R(t)$ too, to get

$$P(Q_f, t_f | Q_i, t_i) = N_o \int DQ_C(t) \int DP_C(t) \delta[P_C(t) - E'(Q_C(t))]$$

$$\times < \delta \left[Q_C(t) - \beta(t) + \int_{t_i}^{t} ds\, I(t-s)\, P_C(s) \right] >_\beta$$

$$= N_o \int_{Q_C(t_i)=Q_i}^{Q_C(t_f)=Q_f} DQ_C(t) < \delta \left[Q_C(t) - \beta(t) + \int_{t_i}^{t} ds\, I(t-s) E'(Q_C(s)) \right] >_\beta \tag{33}$$

This expression tells us that the probability of finding the shift to be Q_f at the time t_f, given that it had a value Q_i at t_i, can be calculated from the stochastic integral equation

$$Q(t) + \int_{t_i}^{t} ds\, I(t-s)\, E'(Q(s)) = \beta(t) \; . \tag{34}$$

Equation (34) is a non-linear, Volterra type integral equation, with an inhomogeneous term, that is random. In arriving at this equation, we had to neglect terms involving higher derivatives of E(Q) than the second. This approximation becomes exact in the limit $\hbar \longrightarrow 0$ as discussed in Section 5.

(4.b) Solving the stochastic integral equation

In this subsection, we discuss the solution of eqn. (34) obeyed by the reaction coordinate Q. The expressions for R(t) and I(t) given in equations (25) and (26) indicate that solving the non-linear integral equation, in general, would be a difficult problem. In certain special cases this can be done. In the high temperature limits, $\beta\hbar\omega \ll 1$ and $\cot(\beta\hbar\omega/2) \simeq 2/\beta\hbar\omega$. Then

$$R(t) \simeq kT \sum_{\upsilon} \frac{G_{\upsilon}^2}{m_{\upsilon}\omega_{\upsilon}^2} \cos(\omega_{\upsilon} t) \tag{35}$$

Hence

$$I(t) = -\frac{1}{kT} \frac{d}{dt} R(t) . \tag{36}$$

Case 1: $\beta(t)$ modelled as white noise. A model that immediately comes into mind is the one in which $\beta(t)$ is taken to be white noise, i.e.

$$R(t-s) = 2E_r kT\,\delta(t-s) \tag{37}$$

where E_r is a constant, which may be taken to be equal to $\sum_\upsilon G_\upsilon^2/m_\upsilon\omega_\upsilon^2$.

Then

$$I(t) = -2E_r\delta'(t) \tag{38}$$

and the integral equation becomes

$$Q(t) + E_r \frac{\partial^2 E}{\partial Q^2}\dot{Q}(t) = \beta(t)\ . \tag{39}$$

This is the equation for Brownian motion of a particle, with mass equal to zero, having position dependent friction, and moving in a potential $1/2Q^2$, the coefficient of friction being $E_r(\partial^2 E/\partial Q^2)$. As this R(t) is a limiting case of the R(t) considered below, we shall not discuss it further.

Case 2: $\beta(t)$ is coloured noise. A more realistic model would be to take

$$R(t) = 2E_r kT\, e^{-\bar{\omega}|t|} \tag{40}$$

Then

$$I(t) = 2E_r\,\bar{\omega}\,\mathrm{sgn}(t)\,e^{-\bar{\omega}|t|} \tag{41}$$

where sgn(t) is the sgn function, defined by sgn(t) = -1 if t < 0, sgn(t) = 1 if t > 0 and sgn(t) = 0 at t = 0.

Equation (40) is equivalent to approximating

$$\sum_{\upsilon} \frac{G_{\upsilon}^{2}}{m_{\upsilon}\omega_{\upsilon}^{2}}\, \delta(\omega - \omega_{\upsilon}) \simeq \frac{2E_{r}\,\bar{\omega}}{\pi(\omega^{2} + \bar{\omega}^{2})} \tag{42}$$

with

$$2E_{r} = \sum_{\upsilon} G_{\upsilon}^{2} / m_{\upsilon}\, \omega_{\upsilon}^{2} \quad . \tag{43}$$

$\bar{\omega}$ determines the width of the function $\sum_{\upsilon} (G_{\upsilon}^{2}/m_{\upsilon}\omega_{\upsilon}^{2})\, \delta(\omega - \omega_{\upsilon})$ and may be approximated by

$$\bar{\omega}^{2} = \frac{\sum_{\upsilon} \frac{G_{\upsilon}^{2}}{m_{\upsilon}\omega_{\upsilon}^{2}}\, \omega^{2}}{\sum_{\upsilon} \frac{G_{\upsilon}^{2}}{m_{\upsilon}\,\omega_{\upsilon}^{2}}} = \frac{\sum_{\upsilon} \frac{G_{\upsilon}^{2}}{m_{\upsilon}}}{2\,E_{r}} \quad . \tag{44}$$

The definition of $2E_{r}$ is identical to that of Schmickler. It is the reorganization energy. With the above choice for R(t), the integral equation (34) can be converted exactly into a differential equation. For this we differentiate equation (34) with respect to t, to obtain

$$\dot{Q} + \int_{t_{i}}^{t} ds \frac{dI(t-s)}{d(t-s)} E'(Q(s)) = \dot{\beta} \tag{45}$$

As I(t) obeys the differental equation

$$\frac{dI(t)}{dt} + \bar{\omega}\, \mathrm{sgn}(t) I(t) = 4E_{r}\, \bar{\omega}\, \delta(t) \tag{46}$$

we get

$$\dot{Q} - \bar{\omega}\int_{0}^{t} I(t-s)E'(Q(s))ds + 2E_r\,\bar{\omega}\,E'(Q(t)) = \dot{\beta}\ . \tag{47}$$

In deriving equation (47), we have taken the physically plausible value of 1/2 for $\int_{t_i}^{t} ds\delta(t-s)$. Using equation (34) in equation (47) to eliminate the term involving the integral, we arrive at

$$\dot{Q} + \bar{\omega}\,Q + 2E_r\bar{\omega}\,E'(Q) = \bar{\omega}\,\beta + \dot{\beta} \tag{48}$$

The above can be written as

$$\frac{\dot{Q}}{2E_r\bar{\omega}} + V'(Q) = \frac{\dot{\beta} + \omega\,\beta}{2E_r\bar{\omega}} \tag{49}$$

where

$$V'(Q) = \frac{\partial V(Q)}{\partial Q} \qquad \text{and} \qquad V(Q) = E(Q) + \frac{Q^2}{4E_r}\ . \tag{50}$$

As $\beta(t)$ is Gaussian with mean zero and autocorrelation $2kTE_r \times e^{-\bar{\omega}|t|}$, it obeys the differential equation

$$\dot{\beta} + \bar{\omega}\,\beta = \sqrt{4\,E_r k\,T\,\bar{\omega}}\;\xi(t)$$

with $\xi(t)$ being white noise with autocorrelation $\delta(t-s)$. So,

$$\frac{\dot{Q}}{2E_r\bar{\omega}} + V'(Q) = \sqrt{\frac{k\,T}{E_r\bar{\omega}}}\;\xi(t)\ . \tag{51}$$

This is the equation for Brownian motion of a particle of mass zero, and friction coefficient $1/(2E_r\bar{\omega})$, moving in a potential

V(Q) subjected to a force which is delta correlated. One can easily derive the Fokker-Planck equation, for the associated distribution function $f(Q, t)$. It is[10]

$$\frac{\partial f(Q, t)}{\partial t} = 2E_r\bar{\omega}\left[\frac{\partial}{\partial Q} V(Q) f(Q, t) + kT \frac{\partial^2}{\partial Q^2} f(Q, t)\right] . \qquad (52)$$

For certain values of $2E_r$ and Δ, the potential V(Q) has a double well structure. The expression for the rate of climbing over the barrier is well known[10]. it is

$$\text{Rate} = \frac{\bar{\omega}}{2\pi}\sqrt{\upsilon(Q_1)|\upsilon(Q_2)|}\; e^{-(\Delta V/kT)} \qquad (53)$$

where

$$\upsilon(Q) = 1 + 2E_r\frac{\partial^2 E(Q)}{\partial Q^2} \qquad (54)$$

and

$$\Delta V = V(Q_2) - V(Q_1) . \qquad (55)$$

Q_1 is the value of Q at which V(Q) is a minimum and near which the particle is located initially. At Q_2, V(Q) is a maximum and the rate in equation (53) is the rate at which the particle jumps over the barrier.

In the rate given in eqn. (53), $\bar{\omega}/2\pi$ is the pre-exponential factor, suggested by Schmickler, in reference 1 (equation 24). Our expression differs from his, in that it has the factor $\sqrt{\upsilon(Q_1)|\upsilon(Q_2)|}$ multiplying $\bar{\omega}/2\pi$. This may be thought as modifying the activation energy, by writing the rate as

$$\text{Rate} = (\bar{\omega}\ /2\pi)\ \exp(-U/kT) \tag{56}$$

$$U = \Delta V - \frac{kT}{2}\ \ln\ \{\upsilon(Q_1)|\upsilon(Q_2)|\}\ . \tag{57}$$

(4.c) The rate for large bandwidth limit

This subsection is included mainly for the sake of completeness. Most equations here are equivalent to those obtained by Schmickler, though occasionally, our expressions are different. If the bandwidth B of the metal is large ($B \gg \Delta$) and if $\Delta(\omega)$ is independent of ω, then, as indicated in Section 3, we have the expressions given in equations (8) and (10) for $\rho_a(\omega, Q)$ and $\langle n_a \rangle$. Because of our eqn. (11), we can write

$$E(Q) = \int^{Q} \langle n_a \rangle\ dQ \tag{58}$$

Performing the integration, leads to

$$E(Q) = \frac{Q}{2} + \frac{1}{\pi}\ (Q + \varepsilon_a - \varepsilon_F)\ \tan^{-1}\left[\frac{\varepsilon_F - \varepsilon_a - Q}{\Delta}\right] + \frac{\Delta}{2\pi}\ \ln\left[(\varepsilon_a + Q - \varepsilon_F)^2 + \Delta^2\right] + C'\ . \tag{59}$$

The constant C' is in fact infinite (as indicated by Schmickler) but that does not worry us as we are interested only in energy differences. Thus,

$$V(Q) = \frac{1}{4E_r}\left[Q + E_r\right]^2 + \frac{(Q + \varepsilon_a - \varepsilon_F)}{\pi} \tan^{-1}\left(\frac{\varepsilon_F - \varepsilon_a - Q}{\Delta}\right)$$

$$+ \frac{\Delta}{2\pi} \ln\left[(\varepsilon_a + Q - \varepsilon_F)^2 + \Delta^2\right] + C \qquad (60)$$

with $C = C' - E_r/4$.

Now we define two new variables, R and η by $R = Q + E_r$ and $\eta = \varepsilon_F - \varepsilon_a + E_r$. Then the potential V is a function of these two, and is given by

$$V(R,\eta) = \frac{R^2}{4E_r} + \frac{R - \eta}{\pi} \tan^{-1}\left(\frac{\eta - R}{\Delta}\right) + \frac{\Delta}{2\pi} \ln\left[(R-\eta)^2 + \Delta^2\right] + C . \qquad (61)$$

The extrema of this equation, considered as a function of the reaction co-ordinate R, are given by

$$\frac{\partial V}{\partial R}(R, \eta) = \frac{R}{2E_r} + \frac{1}{\pi} \tan^{-1}\left(\frac{\eta - R}{\Delta}\right) = 0. \qquad (62)$$

Equation (62) is equivalent to equation (10) of reference 1 and may be derived therefrom. It has at least one solution. If the following two conditions are satisfied, then it has three solutions, corresponding to two minima and one maximum.

$$\frac{2E_r}{\pi\Delta} > 1 \quad \text{and} \quad \frac{2E_r}{\pi} \tan^{-1}\left[\sqrt{\frac{2E_r}{\pi\Delta} - 1}\right] - \Delta\sqrt{\frac{2E_r}{\pi\Delta} - 1} > |\eta| \qquad (63)$$

$\upsilon(Q)$ can easily be calculated to be

$$\upsilon(Q) = 1 - \frac{2E_r}{\pi\left[(\varepsilon_F - \varepsilon_a - Q)^2 + \Delta^2\right]}$$

$$= 1 - 2E_r\rho_a(\varepsilon_F,\ Q)\ . \tag{64}$$

Hence our correction factor to the rate involves *density of states at the Fermi level* for both the minimum (initial state) and the maximum (transition state).

When $\eta(=\varepsilon_F - \varepsilon_a + E_r)$ is zero, the potential is $V(R,0)$ and it is symmetric in R. So the wells have equal depth in this case and the rate of jumping from one well to the other is exactly equal to the rate of jumps in the reverse direction. This is the equilibrium situation. η measures the deviation of the Fermi level from this situation. Hence, η may be identified with the overpotential. Let R_1 and R_3 be the two minima and R_2 the maximum of $V(R,\ \eta)$ and let n_1, n_2 and n_3 be the associated values of $\langle n_a \rangle$. Then ΔV for going from R_1 to R_3 over R_2 is

$$\Delta V = V(R_2,\ \eta) - V(R_1,\ \eta) \tag{65}$$

The symmetry factor is then given by

$$\alpha = \frac{\partial U}{\partial \eta} = \frac{\partial V(R_2,\ \eta)}{\partial \eta} - \frac{\partial V(R_1,\ \eta)}{\partial \eta} - \frac{kT}{2}$$

$$\times \frac{\partial}{\partial \eta} \ln \{\upsilon(Q_2) | \upsilon(Q_1)\}\ . \tag{66}$$

In the above, terms involving $\partial R_i/\partial\eta$ (i = 1, 2) are absent as

$(\partial V(R,\ \eta)/\partial R)_{R_i} = 0$. This leads to

$$\alpha = n_2 - n_1 - \frac{kT}{2} \frac{\partial}{\partial \eta} \ln \{|\upsilon(Q_2)|\upsilon(Q_1)\} \qquad (67)$$

α is obviously η dependent.

The white noise limit can be obtained by letting both $2E_r$ and $\bar{\omega}$ in equation (40) become infinite, with the ratio $2E_r/\bar{\omega}$ kept constant. In this case $\Delta V = \infty$ and then the rate is equal to zero.

(5) DISCUSSION

What we have carried out is an explicit demonstration that the Hamiltonian of equation (1), leads directly to a stochastic integral equation, in appropriate limits. Such a demonstration is interesting in itself as it can be done in rare cases only. Further, we have arrived at an expression for the rate of electron transfer, which has a correction factor to the one given by Schmickler[1].

(5.a) Approximations made in the derivation

Two approximations have been made in arriving at equation (34). First, of course, is the adiabatic approximation. The second is the neglect of terms involving third and higher derivatives of E(Q). This means that if E(Q) is a quadratic function of Q, then equation (34) is exact. For such a potential, all quantum effects, including tunnelling, are accounted for by the stochastic equation; If the behaviour of E(Q) near its maximum is parabolic, then the equation is expected to be a good approximation.

Neglect of the third derivative in equation (34) can be justified when $|E'(Q)/E'''(Q)| \gg 2E_r$ x maximum of $(\hbar\bar{\omega}, kT)$.

(5.b) Inner sphere reactions and other possible extensions

(i) In the above, we considered only the case in which the coupling between the ionic orbital and the solvent is linear in the harmonic oscillator co-ordinates. This approach can easily be extended to the case where the coupling term has the form $f(Q)n_a$ where $f(Q)$ is an arbitrary function of Q. $f(Q)$ can be taken to be quadratic, or perhaps a Morse type of function, and may represent the fact that a local mode is strongly coupled to the electron in the ionic orbital. This can be a model for inner sphere reaction. Equation (51) remains unaltered, but V(Q) is now given by

$$V(Q) = Q^2/4E_r + E(f(Q)) \tag{68}$$

so that the only modification is in the potential in which the particle moves.

(ii) An interesting possibility is the case where one of the G_υs is very large compared to others. This mode is then strongly coupled to the electron. In such a situation, one can take

$$R(t) = 2E_r kT\, e^{-\bar{\omega}\,|t|} + G_0^{\,2} \coth\left[\frac{\beta\hbar\omega_0}{2}\right]\hbar \cos(\omega_0 t) \qquad (69)$$

ω_0 is the frequency of the mode and G_0 its value for G_υ.

(iii) When R(t) is taken as an exponential, its Laplace transform $\phi(s) = \int_0^\infty dt\, R(t)e^{-st} = 2E_r kT/(s+\bar{\omega})$. A more general R(t) for which the Laplace transform is given by $\phi(s) = 2E_r kT/(s+\bar{\omega}+a_1/(s+b_1))$, a_1 and b_1 being constants, can also be handled[11]. In this case, however, the number of stochastic differential equations to be solved is two. In general, if $\phi(s)$ can be approximated at the nth step in a continued fraction expansion for it, then one can convert the integral equation (34) to (n + 1) differential equations.

Since the publication[12] of the work described above, extensions of it have been made. Using a bosonization technique, together with quantum transition state theory, Sebastian[13] showed how the continuum of potential energy surfaces (PES) may be accounted for. The calculations of overpotential dependence of the rate have also been presented. In a recent paper[14], Matyushov *et al* have further developed our work, such that the Gibbs energy of an electrochemical system has been calculated from the Hamiltonian over a wide range of electrode potentials and the rate constant of adiabatic electron transfer has been found for high and low activation energies. In the following chapter, we apply the methods of Sebastian to proton transfer to an electrode, where one expects the continuum of PES to play an important role, as the interaction of nuclear motion with the electronic system is stronger than in electron transfer.

APPENDIX A. Evaluation of a term in equation (23)

Here we consider the evaluation of

$$I = \mathrm{Tr}_e\{U_e(t_f,\ t_i;\ [Q(t)])\ e^{-\beta H_e(Q_i)}\ U_e^{+}(t_f,\ t_i;\ [\tilde{Q}(t)]\}\ .$$

The equation obeyed by $U_e(t,\ t_i;\ [Q(t)])$ is

$$i\hbar \frac{\partial}{\partial t}\ U_e(t,\ t_i;\ [Q(t)]) = H_e(Q(t))\ U_e(t,\ t_i;\ [Q(t)]) \quad . \tag{A.1}$$

We introduce an "adiabatic basis" $|\psi_n(Q(t))>$ which obeyes

$$H_e(Q(t))\ |\psi_n(Q(t))> = E_n(Q(t))\ |\psi_n(Q(t))> \quad . \tag{A.2}$$

It is reasonable to assume that electronic excitation in the metal displaces the potential energy surfaces upwards, by an amount which is independent of $Q(t)$, i.e.

$$E_n(Q(t)) = E(Q(t)) + \Delta E_n \tag{A.3}$$

where $E(Q)$ is the ground state electronic energy and ΔE_n is independent of $Q(t)$. In the limit $\omega_m/\Delta \ll 1$ the motion is adiabatic and this means

$$U_e(t_f,\ t_i;\ [Q(t)])\ |\psi_n(Q_i)> = \exp\left[-\frac{i}{\hbar}\int_{t_i}^{t_f} dt\ E_n(Q(t))\right] |\psi_n(Q_f)> \tag{A.4}$$

with correction terms of order (ω_m/Δ). Using equations (A.3) and

(A.4), we obtain

$$I = \exp\left[- \frac{i}{\hbar} \int dt \; \{ \; E(Q(t)) \; - \; E(\tilde{Q}(t)) \; \} \right] \mathrm{Tr}_e \left(\; e^{-\beta H_e(Q_i)} \; \right)$$

which is the result used in the text.

APPENDIX B .

(1) THE TRANSITION STATE THEORY

It was found possible to formulate a satisfactory theory by focussing attention on the activation complexes, which are the molecular systems whose configurations correspond to the saddle point region on the potential energy surface. In particular this theory arrives at an expression for the concentration of activated complexes through an equilibrium formulation; in a special sense, activated complexes are regarded as being at equilibrium with the reactant molecules. This theory of rates which focusses attention on the activated complexes and calculate their concentrations on the basis of the equilibrium hypothesis is referred as *activated complex theory.* Various other names, including *"absolute rate theory", "the theory of absolute reaction rates"* and *transition state theory*[15], are also used. A clear formulation of the approach was made in 1935 by Eyring[16] and somewhat similar approach leading to the same rate equation was made by Evans and Polanyi[17,18].

The basic rate equation derived by Eyring and by Evans and Polanyi, has been applied to a vast number of chemical reactions of all types and to a number of physical processes such as viscous flow. By and large, it has proved to give very satisfactory interpretation of reaction rates.

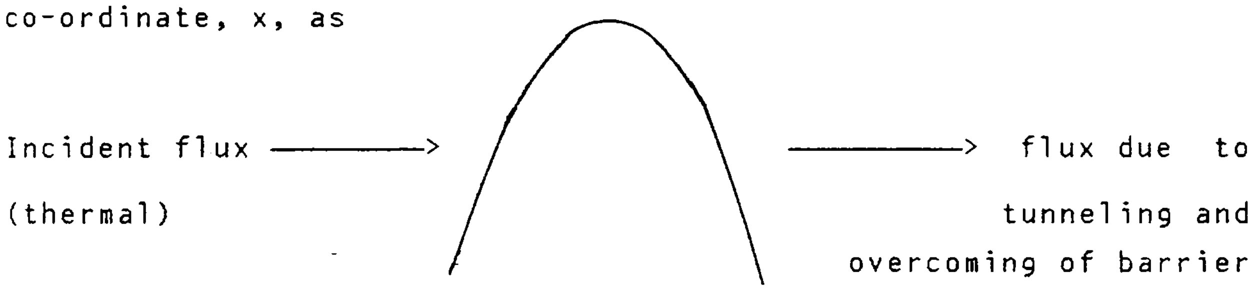
(2) *Quantum Transition State Theory*

It is well recognised that transition state theory provides an extremely useful description of chemical reaction rates. Transition state theory, however, is based inherently on classical mechanics e.g. its "fundamental assumption" is that no classical trajectory crosses the dividing surface that separates reactants and products more than once i.e. the reaction dynamics is direct.

The transition state theory, within the realm of classical mechanics, describes a threshold region which is the energy regime important for determining the thermal rate constant, for chemical reactions with significant activation energy, But the success of classical transition state theory is hollow because quantum effects are also important in the threshold region, particularly so if the reaction dynamics involves light atoms e.g. H atom transfer.

Thus for the reactions involving the light atoms like hydrogen, where barrier over crossing and sub-barrier tunnelling are important, the classical transition state theory has to be modified by including the quantum effects. This version is known as *quantum transition state theory (QTST)* has been discussed by many authors[20-28]. Recently, a interesting simple version of QTST has been applied very successfully in the electrochemical context[28].

In this version an analytical expression can be obtained for the rate, with the approximation that the barrier is well represented by an inverted parabola, along the reaction co-ordinate, x, as



The potential is given by $- 1/2 m\Omega^2 x^2$ and one takes a thermal distribution for the incident flux. The flux coming out on the right hand side due to tunneling and passing over the barrier can be obtained as[19]

$$\Gamma = \frac{kT}{h} \; \frac{\hbar\Omega/2kT}{\mathrm{Sin}\,(\hbar\Omega/2kT)} \qquad (70)$$

In the multidimensional version, this would become,

$$\Gamma = \frac{Q^{\ddagger}}{Q}\left[\frac{k\,T}{h}\;\frac{\hbar\Omega/2kT}{\mathrm{Sin}(\hbar\Omega/2kT)}\right] \qquad (71)$$

where Ω would now be the frequency associated with the reaction co-ordinate in the vicinity of the saddle point.

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CHAPTER IV

DYNAMICS OF PROTON TRANSFER REACTIONS AT METAL ELECTRODES

(1) INTRODUCTION

In the chapter II, we gave the various theoretical methodologies followed by different authors for studying the dynamics of electrochemical proton transfer reactions. In this chapter we present the method that we have developed for the calculation of the rate of the electrochemical proton transfer reaction. Here we study the two limiting cases, adiabatic as well as non-adiabatic. In the case of proton transfer, which is an inner sphere reaction, the interaction of nuclear motion with the electronic system is strong which causes the electron-hole pair excitations to occur in the metal which in turn cause non-adiabaticity. We make use of quantum transition state theory, along with a bosonization technique, for the calculation of the rate.

The role of electron-hole (e-h) excitations in dynamical processes occuring at surfaces has been investigated in the recent past by several authors[1-6]. As the operators corresponding to the creation and annihilation of these obey boson commutation relations approximately, they have been treated as bosons, which makes the analysis of the problem easy. An important conclusion of these investgations is that any process taking place at a metal surface is necessarily non-adiabatic, irrespective of how slowly it is carried out! See reference 6 for a review. Following the procedure of Schönhammer and Gunnarsson[4,5], Sebastian[7] has applied the bosonisation technique to account for e-h excitations in electron transfer. In the case of proton transfer reactions, the problem is more complex (see figure IV). The orbital on H^+ (H_3^+O) which accepts the electron, $|a\rangle$, is coupled to the solvent polarization. Fluctuations in polarization would change the energy of the orbital, by an amount Q. Further, in the reaction, the H^+ ion moves towards the metal, and its position is given by the co-ordinate q. The orbital energy of $|a\rangle$ also depends on q, due to the image interaction, as well as H-H_2O interaction, as is discussed in more detail later.

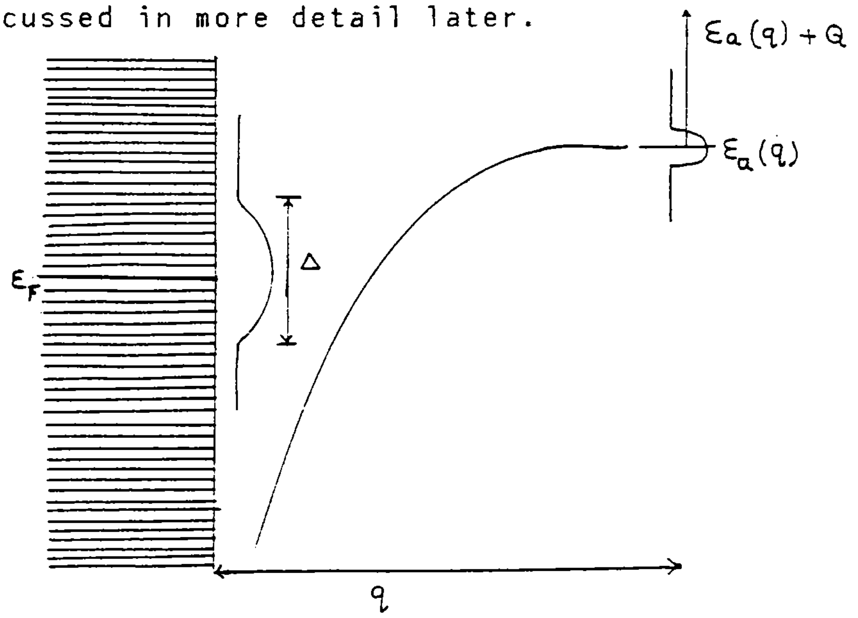

Fig.IV. The electronic energy level of the H_3O^+, ε_a, as a function of the distance from the metal, q. Q represents the shift of the ionic orbital due to the interaction with the solvent. Δ is the width in energy of the ionic orbital. ε_F is the Fermi level of the metal.

Calef and Wolynes (CW)[8], have analysed homogeneous electron transfer reactions. According to them, the reaction co-ordinate is

$$x = \int dr\, \vec{P}(\vec{r}).\left(\vec{E}_o^{1}(\vec{r}) - \vec{E}_o^{2}(\vec{r})\right) \qquad (1)$$

x represents the relative shift of the acceptor orbital's energy with respect to that of the donor orbital, due to the fluctuations in the solvent polarization, $\vec{P}(\vec{r})$ is the polarization of the solvent at the point $\vec{r}$ and $\vec{E}_o^{1}(\vec{r})$ and $\vec{E}_o^{2}(\vec{r})$ are 'bare' electric fields when the electron is located on the donor and acceptor respectively. CW assume x to obey a Langevin equation (LE). This type of problem may also be attacked using an approach in terms of a Hamiltonian, as shown by several authors (see Pollak *et al*[9] and the references therein and Sebastian and Ananthapadmanabhan[10]). The problem of electrochemical proton transfer is more complicated than electron transfer, and correspondingly, the Hamiltonian also is more complex.

(2) THE HAMILTONIAN

We consider a modified version of the Newns-Anderson Hamiltonian[11,12]

$$H = H_e(Q,\, q) + 1/2 \sum_{\upsilon}\left[p_{\upsilon}^2 + \omega_{\upsilon}^2\, q_{\upsilon}^2\right] + p^2/2m + V_o(q) \qquad (2)$$

which accounts for all the points raised in the introduction. In this Hamiltonian, the solvent is represented as a collection of harmonic oscillators, the υth oscillator's position being denoted by q_υ, momentum by p_υ and frequency by ω_υ. $H_e(Q, q)$ is the Hamiltonian for electronic system. It depends on positions q_υ of the harmonic oscillators through Q, defined by $Q = \sum_\upsilon C_\upsilon q_\upsilon$, C_υ being constants. Q is the shift of the energy of the ionic orbital, due to its coupling to the harmonic oscillators. It also depends on the distance, q of the H^+ ion from the metal electrode surface. Explicitly,

$$H_e(Q, q) = \sum_\sigma \varepsilon_a(q)\, n_{a\sigma} + \sum_{k,\sigma} \varepsilon_k\, n_{k\sigma} + \sum_{k,\sigma} \Big[V_{ak}(q)\, C^+_{a\sigma} C_{k\sigma} + V_{ka}(q) \times C^+_{k\sigma} C_{a\sigma} \Big] + \sum_\sigma Q\, n_{a\sigma} + U(q)\, n_{a\uparrow} n_{a\downarrow} \qquad (3)$$

The solid is described in one electron model and ε_k are the energies of one electron states of the solid. $V_{ak}(q)$ is the hopping term causing electron transfer and $V_{ka}(q)$ is its complex conjugate. U(q) stands for electron-electron repulsion and σ stands for spin . $C_{a\sigma}$ and $C_{k\sigma}$ ($C^+_{a\sigma}$ and $C^+_{k\sigma}$) are annihilation (creation) operators for one electron states $|a\sigma\rangle$ and $|k\sigma\rangle$ respectively. $n_{a\sigma}$ and $n_{k\sigma}$ are corresponding occupation number operators. The term $Qn_{a\sigma}$ accounts for the fact that the equilibrium positions of the harmonic oscillators are changed by transfer of the electron.

We adopt the Hartree-Fock (HF) approximation, as this is expected to describe the reaction satisfactorily. The two electron interaction term $n_{a\uparrow}n_{a\downarrow}$ is now replaced by $n_{a\uparrow}\langle n_{a\downarrow}\rangle$ + $\langle n_{a\uparrow}\rangle n_{a\downarrow}$ - $\langle n_{a\uparrow}\rangle\langle n_{a\downarrow}\rangle$. This gives

$$H_{e,HF}(Q, q) = \sum_{\sigma} \left[\varepsilon_a(q) + Q + U(q) < n_{a\bar{\sigma}} > \right] n_{a\sigma} + \sum_{k,\sigma} \varepsilon_k n_{k\sigma}$$

$$+ \sum_{k,\sigma} \left[V_{ak}(q) C^{+}_{a\sigma} C_{k\sigma} + V_{ka}(q) C^{+}_{k\sigma} C_{a\sigma} \right] - U(q)\langle n_{a\uparrow}\rangle\langle n_{a\downarrow}\rangle \tag{4}$$

$$= \sum_{\sigma} \varepsilon_{a\sigma}(Q, q) n_{a\sigma} + \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{k,\sigma} \left[V_{ak}(q) C^{+}_{a\sigma} C_{k\sigma} \right.$$

$$\left. + V_{ka}(q) C^{+}_{k\sigma} C_{a\sigma} \right] - U(q)\langle n_{a\uparrow}\rangle\langle n_{a\downarrow}\rangle \tag{5}$$

where

$$\varepsilon_{a\sigma}(Q, q) = \varepsilon_a(q) + Q + U(q) \langle n_{a\bar{\sigma}} \rangle . \tag{6}$$

Further, we shall put the condition of restricted Hartree-Fock viz. $\langle n_{a\uparrow}\rangle = \langle n_{a\downarrow}\rangle$ so that $\varepsilon_{a\uparrow} = \varepsilon_{a\downarrow}$. $\varepsilon_{a\sigma}(Q, q)$ is the effective energy of $|a\sigma\rangle$, which may take up one electron from the metal. The change of the distance between the ion and the electrode, q, will also change ε_a due to image interaction. So ε_a is a function of q. The explicit dependence of ε_a on q will be given later (see equation (95)). The metal is now described by a one-electron Hamiltonian. For the electron transfer to occur, the value of Q has to change so that the quantity $\varepsilon_{a\sigma}(Q, q)$ which is the effective energy of the orbital $|a\sigma\rangle$ crosses the Fermi level ε_F. $V_o(q)$ is a potential energy term, (which has no dependence on electronic co-ordinates (see equation (100)) of the H^+ ion and $p^2/2m$ is its kinetic energy.

(3) THE LOWEST POTENTIAL ENERGY SURFACE

If the electronic system is in the ground adiabatic Hartree-Fock state with energy $E_{o,HF}(Q, q)$, which obeys

$$H_{e,HF}(Q, q)\ |\psi_o\rangle = E_{o,HF}(Q, q)\ |\psi_o\rangle\ , \tag{7}$$

then nuclear motion will take place under the influence of a potential $V(g, q)$ which is the sum of the harmonic oscillator potentials $1/2 \sum_{\upsilon}\omega_{\upsilon}^{2} q_{\upsilon}^{2}$, the electronic energy $E_{o,HF}(Q, q)$ and the potential in which ion moves, $V_o(q)$.

$$V(\underset{\sim}{g}, q) = 1/2 \sum_{\upsilon} \omega_{\upsilon}^{2} q_{\upsilon}^{2} + E_{o,HF}(Q, q) + V_o(q) \tag{8}$$

where $g = (q_1, q_2, \ldots\ldots q_N)$. We now find the the extrema of this potential. They are determined by

$$\frac{\partial V(g, q)}{\partial q_{\upsilon}} = \omega_{\upsilon}^{2}\ q_{\upsilon} + E'_{o,HF}(Q, q)\ C_{\upsilon} = 0 \tag{9}$$

with $E'_{o,HF}(Q, q) = \dfrac{\partial E_{o,HF}(Q, q)}{\partial Q}$

and

$$\frac{\partial V(g, q)}{\partial q} = \frac{\partial V_o(q)}{\partial q} + \frac{\partial E_{o,HF}(Q, q)}{\partial q} = 0. \tag{10}$$

$V(g, q)$ is an extremum at $g = (q_{1\alpha}, q_{2\alpha}, \ldots\ldots q_{N\alpha})$ where $\alpha =$ (1, 2, ...) takes as many values as there are extrema.

Equation (9) may be rewritten as

$$q_{\upsilon\alpha} = - \frac{E'_{o,HF}(Q_\alpha, q_\alpha)}{\omega_\upsilon^2} \tag{11}$$

which when substituted into

$$Q_\alpha = \sum_\upsilon C_\upsilon \, q_{\upsilon\alpha} \tag{12}$$

gives

$$\frac{Q_\alpha}{2E_r} + E'_{o,HF}(Q_\alpha, q_\alpha) = 0 \tag{13}$$

where

$$2E_r = \sum_\upsilon \frac{C_\upsilon^2}{\omega_\upsilon^2} \tag{14}$$

with E_r being the reorganisation energy. Equations (10) and (13) may be rewritten as

$$\left[\frac{\partial U(Q, q)}{\partial q}\right]_{q = q_\alpha} = 0 \quad \text{and} \quad \left[\frac{\partial U(Q, q)}{\partial Q}\right]_{Q = Q_\alpha} = 0$$

where

$$U(Q, q) = \frac{Q^2}{4E_r} + E_{o,HF}(Q, q) + V_o(q) \; . \tag{15}$$

One can easily prove that the potential at the extremum is equal to the value of U(Q, q) at its extremum.

The expression for $E_{o,HF}(Q, q)$ may be evaluated numerically, as discussed later. Our interest is only in cases where U(Q, q) has three extrema corresponding to (Q_1, q_1), $(Q_2,$

q_2) and (Q_3, q_3). Here (Q_1, q_1) and (Q_3, q_3) correspond to minima of $V(\underline{q}, q)$ while (Q_2, q_2) corresponds to the saddle point. We take the occupation numbers of the orbital $|a\sigma\rangle$ corresponding to (Q_1, q_1), (Q_2, q_2) and (Q_3, q_3) obey $\langle n_{a\sigma}(Q_1, q_1)\rangle < \langle n_{a\sigma}(Q_2, q_2)\rangle < \langle n_{a\sigma}(Q_3, q_3)\rangle$. We identify these as the reactant, the saddle and the product, respectively.

(4) THE ADIABATIC DENSITY OF STATES $\rho_a^\sigma(\varepsilon, Q, q)$

In the following we shall make extensive use of adiabatic one electron state $|\psi_{m\sigma,Q,q}\rangle$ of the Hamiltonian $H_{1,HF}(Q, q)$, having eigen values $\varepsilon_{m\sigma}$ which obey

$$H_{1,HF}(Q, q)\ |\psi_{m\sigma}, Q, q\rangle = \varepsilon_{m\sigma}\ |\psi_{m\sigma}, Q, q\rangle \qquad (16)$$

where

$$H_{1,HF}(Q, q) = \sum_\sigma \varepsilon_{a\sigma}(Q, q) n_{a\sigma} + \sum_{k,\sigma}\left[\varepsilon_k n_{k\sigma} + V_{ak}(q) C^+_{a\sigma} C_{k\sigma} + V_{ka}(q) C_{k\sigma} C^+_{a\sigma}\right] \qquad (17)$$

A very useful quantity is $\rho_a^\sigma(\varepsilon, Q, q)$, the adiabatic density of states of the orbital, $|a\sigma\rangle$, which is defined by

$$\rho_a^\sigma(\varepsilon, Q, q) = \sum_m |\langle a\sigma|\psi_{m\sigma}, Q, q\rangle|^2\ \delta\ (\varepsilon - \varepsilon_m) \qquad (18)$$

$$= -\frac{1}{\pi}\ \text{Imaginary part of } G^\sigma_{aa}(\varepsilon) \qquad (19)$$

where

$$G^\sigma_{aa}(\varepsilon) = \langle a\sigma|(\varepsilon + i\alpha - H_{1,HF}(Q, q))^{-1}|a\sigma\rangle \qquad (20)$$

where α is an infinitesimal positive quantity which tends to zero. $G_{aa}^{\sigma}(\varepsilon)$ can be easily determined, as $H_{1,HF}(Q, q)$ is a one electron Hamiltonian. Defining

$$\Delta(\varepsilon, q) = \pi \sum_{k} | V_{ak}(q)|^2 \delta (\varepsilon - \varepsilon_k) \tag{21}$$

to be a weighted density of states function, one can obtain[12]

$$G_{aa}^{\sigma}(\varepsilon) = \left[\varepsilon - \varepsilon_{a\sigma}(Q, q) - \Pi(\varepsilon, q) + i\Delta(\varepsilon, q)\right] , \tag{22}$$

where

$$\Pi(\varepsilon, q) = \frac{1}{\pi}\left[\text{principal value of } \int_{-\infty}^{\infty} \frac{\Delta(\varepsilon_1, q)\, d\varepsilon_1}{(\varepsilon - \varepsilon_1)}\right] . \tag{23}$$

If the metal is taken to have a finite band width, then $\rho_a^{\sigma}(\varepsilon, Q, q)$ is obtained as[13]

$$\rho_a^{\sigma}(\varepsilon, Q, q) = \frac{\Delta(\varepsilon, q)}{\pi\left[(\varepsilon-\varepsilon_{a\sigma}(Q, q)- \Pi(\varepsilon, q))\right]^2 + \Delta^2(\varepsilon, q)\left.\right]} . \tag{24}$$

(5) RATE IN THE ADIABATIC LIMIT

We now calculate the rate of electron transfer using the quantum transition state theory, (QTST), assuming that the motion takes place on the lowest potential energy surface V(g, q). In order to evaluate the rate using QTST, we expand the potential energy as a Taylor series in the vicinity of each extremum. Thus we have

$$V(g, q) = V_{\alpha} + \delta^{2}V_{\alpha} \tag{25}$$

where

$$V_\alpha = E_{o,HF}(Q_\alpha, q_\alpha) + 1/2 \sum_\upsilon \omega_\upsilon^2 q_{\upsilon\alpha}^2 + V_o(q_\alpha) \qquad (26)$$

and

$$\delta^2 V_\alpha = 1/2 \sum_\upsilon \omega_\upsilon^2 \, \delta q_\upsilon^2 + 1/2\, E_{o,HF}''(Q_\alpha, q_\alpha)\, \delta Q^2$$
$$+ 1/2\left[\frac{\partial^2 V_o(q_\alpha)}{\partial q^2}\right]\delta q^2 + 1/2\left[\frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial q^2}\right]\delta q^2$$
$$+ 1/2\left[\frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial Q\, \partial q}\right]\delta Q\, \delta q \qquad (27)$$

where

$$\delta q_\upsilon = q_\upsilon - q_{\upsilon\alpha} \; ; \; \delta Q = Q - Q_\alpha \quad \text{and} \quad E_o''(Q_\alpha, q_\alpha) = \left[\frac{\partial^2 E_o(Q_\alpha, q_\alpha)}{\partial Q^2}\right] .$$

The Hamiltonian for solvent oscillators may be approximated as H_α where

$$H_\alpha = 1/2 \sum_\upsilon p_\upsilon^2 + V_\alpha + \delta^2 V_\alpha \qquad (28)$$

H_α is the Hamiltonian for a collection of harmonic oscillators. For $\alpha = 1$ or 3 all the modes are stable as $q_{\upsilon\alpha}$ corresponds to a minimum. As $\alpha = 2$, corresponds to the saddle, one mode is unstable. This is the reaction co-ordinate. We shall denote its frequency by Ω_a, `a' standing for adiabatic. The frequency of the normal modes are denoted as $\omega_{\upsilon\alpha}$ and we take ω_{12} to be the unstable mode and put $\omega_{12} = i\Omega_a$. Ω_a is determined by the equation, (see Appendix B for details)

$$\left[\frac{\left[\frac{\partial^2 E_{o,HF}(Q_\alpha,\, q_\alpha)}{\partial Q\, \partial q}\right]}{\left[\Omega_a^{\,2} + \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial^{\,2} E_{o,HF}(Q_\alpha,\, q_\alpha)}{\partial q^2}\right]} - \left[\frac{\partial^2 E_{o,HF}(Q_\alpha,\, q_\alpha)}{\partial Q^2} \right] \right]$$

$$\times \frac{2}{\pi} \int_0^\infty \frac{\omega\ J(\omega)\ d\omega}{(\Omega_a^{\,2} + \omega^2)} = 1 \qquad (29)$$

where we have defined the solvent spectral function, $J(\omega)$ by

$$J(\omega) = \frac{\pi}{2} \sum_\upsilon C_\upsilon^{\,2}/\omega_\upsilon \quad \delta(\omega - \omega_\upsilon)\ . \qquad (30)$$

The QTST expression for the rate is [14]

$$\Gamma_a = \frac{\Omega_a}{2\pi\ \mathrm{Sin}\left[\frac{\Omega_a}{2kT}\right]} \cdot \frac{\prod_\upsilon \ \sinh\left[\frac{\omega_{\upsilon 1}}{2kT}\right]}{\prod_\upsilon{}' \ \sinh\left[\frac{\omega_{\upsilon 2}}{2kT}\right]} \ \exp\,(-\Delta V/kT) \qquad (31)$$

where $\Delta V = V_2 - V_1$. The prime in $\prod_\upsilon{}'$ indicates that the unstable mode has to be left out. In equation (31) we have put $\hbar = 1$. The products of sinh functions are simply partition functions for the initial and transition states. Using the infinite product representation for the sin and sinh functions

$$\sinh x = x \prod_{n=1}^{\infty} \left[1 + \frac{x^2}{n^2\ \pi^2} \right] \qquad (32)$$

$$\sin x = x \prod_{n=1}^{\infty} \left[1 - \frac{x^2}{n^2\ \pi^2} \right] \qquad (33)$$

we write Γ_a as

$$\Gamma_a = \frac{\Omega_a}{2\pi} \sqrt{|p_o|} \left[\prod_{n=1}^{\infty} p_n \right] \exp(-\Delta V/kT) \tag{34}$$

where

$$p_n = \frac{\prod_{\upsilon} (n^2 + Z^2 \omega_{\upsilon 1}^2)}{(n^2 - Z^2 \Omega_a^2) \prod_{\upsilon}' (n^2 + Z^2 \omega_{\upsilon 2}^2)} \tag{35}$$

$Z = 1/2\pi kT$. ln p_n can be written as a trace and analysed to obtain (see Appendix B)

$$p_n = \frac{X_1(n)}{X_2(n)}$$

with

$$X_\alpha(n) = 1 + E''_{o,HF}(Q_\alpha, q_\alpha) \frac{2}{\pi} \int_0^\infty \frac{d\omega \ \omega \ J(\omega)}{\omega^2 + (nZ^{-1})^2} + \left(\bar{N}_\alpha^2 + (nZ^{-1})^2 \right)^{-1}$$

$$\times \ E''_{o,HF}(Q_\alpha, q_\alpha) \ \bar{C}_\alpha^2 \tag{36}$$

where

$$\bar{C}_\alpha^2 = \left[\frac{B(Q_\alpha, q_\alpha)}{E''_{o,HF}(Q_\alpha, q_\alpha)} \right]^2$$

$$\bar{N}_\alpha^2 = \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial q^2} - \frac{B^2(Q_\alpha, q_\alpha)}{E''_{o,HF}(Q_\alpha, q_\alpha)}$$

and

$$B(Q_\alpha, q_\alpha) = \frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial Q \ \partial q} .$$

Further progress can be made only if one assumes a model for $J(\omega)$. If we give a Drude form for $J(\omega)$[7]

$$J(\omega) = \frac{\lambda\ \omega}{\omega_D} \left[1 + (\omega/\omega_D)^2 \right]^{-1} \tag{37}$$

we get

$$X_\alpha(n) = 1 + E''_{o,HF}(Q_\alpha,\ q_\alpha) \frac{2E_r Z\ \omega_D}{(n + Z\omega_D)} + \left[\bar{N}_\alpha^2 + (nZ^{-1})^2 \right]$$

$$\times\ E''_{o,HF}(Q_\alpha,\ q_\alpha)\ \bar{C}_\alpha^2 \quad . \tag{38}$$

Carrying out two differentiations of $E_{o,HF}(Q,\ q)$, we get

$$E''_{o,HF}(Q_\alpha,\ q_\alpha) = \sum_\sigma \frac{\partial\langle n_{a\sigma}\rangle}{\partial Q} \quad .$$

The expression for p_o is

$$p_o = \left| \frac{1 - 2E_r E''_{o,HF}(Q_1,\ q_1) - \left[\bar{C}_1^2 / \bar{N}_1^2 \right] E''_{o,HF}(Q_1,\ q_1)}{1 - 2E_r E''_{o,HF}(Q_2,\ q_2) - \left[\bar{C}_2^2 / \bar{N}_2^2 \right] E''_{o,HF}(Q_2,\ q_2)} \right|^{1/2} \tag{39}$$

The rate becomes

$$\Gamma_a = \frac{\Omega_a}{2\pi} \left| \frac{1 - 2E_r E''_{o,HF}(Q_1,\ q_1) - \left[\bar{C}_1^2 / \bar{N}_1^2 \right] E''_{o,HF}(Q_1,\ q_1)}{1 - 2E_r E''_{o,HF}(Q_2,\ q_2) - \left[\bar{C}_2^2 / \bar{N}_2^2 \right] E''_{o,HF}(Q_2,\ q_2)} \right|^{1/2}$$

$$\times \left[\prod_{n=1}^{\infty} p_n \right] \exp\ (-\Delta V/kT) \quad . \tag{40}$$

The infinite product can be evaluated . Ω can be found to obey a cubic equation if one takes the Drude form for $J(\omega)$. The equation is

$$\Omega_a^{3}\,\omega_D^{-1} + \Omega_a^{2} + \left[\frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial q^2} + \frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial Q\ \partial q}\right]$$

$$\times\Omega_a\omega_D^{-1} + \left[\frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial q^2}\right]\frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial Q^2} - \frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial Q\ \partial q}$$

$$= 0\ . \tag{41}$$

Thus the rate for the proton transfer reaction in the adiabatic limit becomes

$$\Gamma_a = \frac{\Omega_a}{2\,\pi}\sqrt{\frac{1 - 2E_r E''_{o,HF}(Q_1,\ q_1) - \left[\bar{C}_1^2 /\ \bar{N}_1^2\right]\ E''_{o,HF}(Q_1,\ q_1)}{1 - 2E_r E''_{o,HF}(Q_2,\ q_2) - \left[\bar{C}_2^2\ /\ \bar{N}_2^2\right]\ E''_{o,HF}(Q_2,\ q_2)}}$$

$$\times\ \frac{\Gamma(1-iZ\bar{N}_1)\ \Gamma(1+iZ\bar{N}_1)}{\Gamma(1-iZ\bar{N}_2)\ \Gamma(1+iZ\bar{N}_2)}\ \prod_{i=1}^{3}\frac{\Gamma(1-ZK_i^2\ )}{\Gamma(1-ZK_i^1\ )}\ \exp\ (-\Delta V/kT)\ . \tag{42}$$

In the above $\prod_{n=1}^{\infty} p_n$ has been rewritten in terms of Gamma function. K_i^α are the roots of the equation $X_\alpha(ZK) = 0$. This equation written out in detail gives

$$\left[K^2 + \bar{N}_\alpha^{2} + E''_{o,HF}(Q_\alpha,\ q_\alpha)\ \bar{C}_\alpha^{2}\right]\left[K + \omega_D\right] + 2E_r\ E''_{o,HF}(Q_\alpha,\ q_\alpha)\omega_D$$

$$\times\left[K^2 + \bar{N}_\alpha^{2}\right] = 0 \tag{43}$$

This is a cubic equation in K and its roots can be found out analytically, So the rate Γ_a can be evaluated.

In a metal there is a continuum of allowed energy levels in which the electrons can occupy. Muller-Hartmann, Ramakrishnan and Toulose (MHRT)[3] have showed that the switching on of a localised potential will always leave the metal in an excited state, irrespective of how slowly it is done, thus indicating that processes occuring at metal surfaces have to be nonadiabatic. Schotte and Schotte[1], Tomonaga[2], Schönhammer and Gunnarsson[4,5] have shown that these electron-hole (e-h) excitations can be treated as bosons. This approach is justifiable in electrochemical reactions like electrochemical proton transfer because the probability of creating any boson (e-h excitation) is $\ll 1$ as the dynamics of the nuclei are much slower than the dynamics of electronic motion in the metal.

We have derived an expression for rate of proton transfer reaction, accounting for non-adiabaticity in the transfer, using an extension of a procedure followed by Sebastian[7].

(6) THE BOSONISATION

The basic idea is to replace $H_{e,HF}(Q, q)$ in equation (2) by an operator for a collection of bosons. So following MHRT[3] and

Schönhammer and Gunnarsson[4,5] we replace $H_{e,HF}(Q, q)$ by $H_b(Q, q) + E_{o,HF}(Q, q)$,
where

$$H_b(Q, q) = \sum_{j,\sigma} \epsilon_j \, b^+_{j\sigma Q,q} \, b_{j\sigma Q,q} = \sum_{j,\sigma} \epsilon_j \, b^+_{j\sigma\vec{Q}} \, b_{j\sigma\vec{Q}} \quad . \tag{44}$$

For convenience, we introduce a two dimensional vector $\vec{Q}$ with components Q and q. $b^+_{j\sigma\vec{Q}}$ ($b_{j\sigma\vec{Q}}$) creates (annihilates) jth e-h excitation for spin σ in which an electron has been excited from $|\psi_{m_<\sigma\vec{Q}}\rangle\rangle$ with $\varepsilon_{m_<} < \varepsilon_F$ to $|\psi_{m_>\sigma\vec{Q}}\rangle\rangle$ having $\varepsilon_{m_>} > \varepsilon_F$. j stands for a pair $(m_>, m_<)$ and $\epsilon_j = \varepsilon_{m_>} - \varepsilon_{m_<}$. Here $b^+_{j\sigma\vec{Q}}$ and $b_{j\sigma\vec{Q}}$ are Q dependent as $|\psi_{m\sigma\vec{Q}}\rangle\rangle$ are adiabatic states. They will not commute with p_υ. So $H_b(Q, q)$ is written in terms of $b^+_{j\sigma\vec{Q}_o}$ and $b_{j\sigma\vec{Q}_o}$, where $\vec{Q}_o$ is a fixed value of $\vec{Q}$. We shall denote $b^+_{j\sigma\vec{Q}_o}$ and $b_{j\sigma\vec{Q}_o}$ simply as $b^+_{j\sigma}$ and $b_{j\sigma}$. This will commute with p_υ and q_υ. The relationship between $b_{j\sigma\vec{Q}}$ and $b_{j\sigma}$ can be found using a procedure due to Schönhammer and Gunnarsson[4,5]. Differentiating $H_{e,HF}(Q, q)$ with respect to Q, we obtain $\left[\partial H_{e,HF}(Q, q)/\partial Q\right] = \sum_\sigma n_{a\sigma}(Q, q)$. Expressing $n_{a\sigma}$ in terms of $\psi^+_{m\sigma\vec{Q}}$ and $\psi_{m\sigma\vec{Q}}$ which are annihilation and creation operators for $|\psi_{m\sigma\vec{Q}}\rangle\rangle$,
we obtain

$$\frac{\partial H_{e,HF}(\vec{Q})}{\partial Q} = \sum_{m,m',\sigma} \langle \psi_{m\sigma\vec{Q}} | a\sigma \rangle \langle a\sigma | \psi_{m'\sigma\vec{Q}} \rangle \, \psi^+_{m\sigma\vec{Q}} \, \psi_{m'\sigma\vec{Q}} \tag{45}$$

In the spirit of boson approximation, we replace the above by

$$\frac{\partial H_{e,HF}(\vec{Q})}{\partial Q} = \sum_{j,\sigma} F_{j\sigma}(\vec{Q}) \left[b_{j\sigma\vec{Q}} + b^{+}_{j\sigma\vec{Q}} \right] + \frac{\partial E_{o,HF}(\vec{Q})}{\partial Q} . \tag{46}$$

Similarly

$$\frac{\partial H_{e,HF}(\vec{Q})}{\partial q} = \sum_{j,\sigma} F_{j\sigma}(\vec{Q}) \frac{\partial \varepsilon_{a\sigma}(Q,\ q)}{\partial q} \left[b_{j\sigma\vec{Q}} + b^{+}_{j\sigma\vec{Q}} \right] + \frac{\partial E_{o,HF}(\vec{Q})}{\partial q} \tag{47}$$

where

$$F_{j\sigma}(\vec{Q}) = \langle \psi_{m_{<}\sigma\vec{Q}} \mid a\sigma\rangle \langle a\sigma \mid \psi_{m_{>}\sigma\vec{Q}} \rangle . \tag{48}$$

Combining the two equations (46) and (47) we can write

$$\begin{aligned}\nabla H_{e}(\vec{Q}) = {} & \vec{i} \left[\sum_{j,\sigma} F_{j\sigma}(\vec{Q}) \left(b_{j\sigma\vec{Q}} + b^{+}_{j\sigma\vec{Q}} \right) + \frac{\partial E_{o,HF}(\vec{Q})}{\partial Q} \right] \\ & + \vec{j} \left[\sum_{j,\sigma} F_{j\sigma}(\vec{Q}) \left(b_{j\sigma\vec{Q}} + b^{+}_{j\sigma\vec{Q}} \right) \right] \frac{\partial \varepsilon_{a\sigma}(Q,q)}{\partial q} + \frac{\partial E_{o,HF}(\vec{Q})}{\partial q}\end{aligned} \tag{49}$$

$$= \sum_{j,\sigma} \vec{F}_{j\sigma}(\vec{Q}) \left(b_{j\sigma\vec{Q}} + b^{+}_{j\sigma\vec{Q}} \right) + \nabla E_{o,HF}(\vec{Q}) \tag{50}$$

where we use the notation

$$\nabla = \vec{i} \frac{\partial}{\partial Q} + \vec{j} \frac{\partial}{\partial q}$$

and

$$\vec{F}_{j\sigma}(\vec{Q}) = \vec{i}\ F_{j\sigma}(\vec{Q}) + \vec{j}\ F_{j\sigma}(\vec{Q}) \frac{\partial \varepsilon_{a\sigma}(Q,\ q)}{\partial q} .$$

Now differentiating $H_{b}(\vec{Q})$ with respect to Q and q, we get

$$\nabla H_{b}(\vec{Q}) = \sum_{j,\sigma} \epsilon_{j} \left[\nabla b^{+}_{j\sigma\vec{Q}}\ b_{j\sigma\vec{Q}} + b^{+}_{j\sigma\vec{Q}}\ \nabla b_{j\sigma\vec{Q}} \right] + \nabla E_{o,HF}(\vec{Q}) . \tag{51}$$

Comparing the result with equation (49), we obtain

$$\nabla b_{j\sigma\vec{Q}} = \frac{\vec{F}_{j\sigma}(\vec{Q})}{\epsilon_j} \tag{52}$$

so that

$$b_{j\sigma\vec{Q}} = b_{j\sigma\vec{Q}_o} + \epsilon_j^{-1} \int_{\vec{Q}_o}^{\vec{Q}} \vec{F}_{j\sigma}(\vec{Q})\, d\vec{Q} \tag{53}$$

It is easy to prove that $\int_{\vec{Q}_o}^{\vec{Q}} \vec{F}_{j\sigma}(\vec{Q})\, d\vec{Q}$ is independent of the path connecting $\vec{Q}_o$ to $\vec{Q}$. So we put

$$S_{j\sigma}(\vec{Q}) = \epsilon_j^{-1} \int_{\vec{Q}_o}^{\vec{Q}} \vec{F}_{j\sigma}(\vec{Q})\, d\vec{Q} \quad ,$$

and the expression for $b_{j\sigma\vec{Q}}$ becomes

$$b_{j\sigma\vec{Q}} = b_{j\sigma} + S_{j\sigma}(\vec{Q}) \ . \tag{54}$$

If we use this expression for $b_{j\sigma\vec{Q}}$ in the equation (44) we obtain

$$H_b(\vec{Q}) = \sum_{j,\sigma} \left[\epsilon_j\, b^+_{j\sigma}\, b_{j\sigma} + S_{j\sigma}(\vec{Q}) \left(b_{j\sigma} + b^+_{j\sigma} \right) + \frac{S^2_{j\sigma}(\vec{Q})}{\epsilon_j} \right] . \tag{55}$$

Thus the bosonised version of total Hamiltonian may be written as

$$H = 1/2 \sum_{\upsilon} p_{\upsilon}^2 + p^2 + V(g,\ q) + H_b(\vec{Q}) \tag{56}$$

where

$$V(g,\ q) = 1/2 \sum_{\upsilon} \omega_{\upsilon}^2\, q_{\upsilon}^2 + V_o(q) + E_{o,HF}(\vec{Q}) \ . \tag{57}$$

Introducing "position" and "momentum" for the e-h bosons as

$$x_{j\sigma} = (2\epsilon_j)^{-1/2} \left(b_{j\sigma} + b^{+}_{j\sigma} \right) \tag{58}$$

and

$$p_{j\sigma} = -i (\epsilon_j/2)^{1/2} \left(b_{j\sigma} - b^{+}_{j\sigma} \right) \tag{59}$$

we obtain

$$H = 1/2 \sum_{\upsilon} p_{\upsilon}^2 + p^2/2 + 1/2 \sum_{j,\sigma} p_{x_{j\sigma}}^{\;2} + V(\underline{x}, g, q) - 1/2 \sum_{j,\sigma} \epsilon_j \tag{60}$$

where

$$\underline{x} = (x_{1\sigma}, x_{2\sigma}, x_{3\sigma}, \ldots\ldots x_{m\sigma})$$

and

$$V(\underline{x}, g, q) = 1/2 \sum_{j,\sigma} \epsilon_j^2 x_{j\sigma}^{\;2} + 1/2 \sum_{\upsilon} \omega_{\upsilon}^{\;2} q_{\upsilon}^{\;2} + \sum_{j,\sigma} \frac{S^{2}_{j\sigma}(\overline{Q}^{>})}{\epsilon_j} + \sum_{j,\sigma} S_{j\sigma}(\overline{Q}^{>})$$

$$\times \sqrt{2\epsilon_j}\; x_{j\sigma} + V_0(q) + E_{0,HF}(\overline{Q}^{>}) \; . \tag{61}$$

Since $-1/2 \sum_{j,\sigma} \epsilon_j$ is a constant, we omit this term.

(7) RATE IN THE NON-ADIABATIC LIMIT

We now find the extrema of the potential $V(\underline{x}, g, q)$. The coordinates $q_{\upsilon\alpha}$, q_{α} and $x_{j\sigma\alpha}$ of the extremum α obey,

$$\omega_\upsilon^2\, q_{\upsilon\alpha} + \sum_{j,\sigma} \frac{2}{\epsilon_j}\, S_{j\sigma}(\vec{\overline{Q}}_\alpha)\, \frac{\partial S_{j\sigma}(\vec{\overline{Q}}_\alpha)}{\partial q_\upsilon}\, C_\upsilon + \sum_{j,\sigma} \frac{\partial S_{j\sigma}(\vec{\overline{Q}}_\alpha)}{\partial q_\upsilon} \sqrt{2\,\epsilon_j}\; C_\upsilon\, x_{j\sigma\alpha}$$

$$+ \frac{\partial E_{o,HF}(\vec{\overline{Q}}_\alpha)}{\partial Q}\, C_\upsilon = 0 \tag{62}$$

$$\sum_{j,\sigma} \frac{2}{\epsilon_j}\, S_{j\sigma}(\vec{\overline{Q}}_\alpha)\, \frac{\partial S_{j\sigma}(\vec{\overline{Q}}_\alpha)}{\partial q} + \sum_{j,\sigma} \frac{\partial S_{j\sigma}(\vec{\overline{Q}}_\alpha)}{\partial q} \sqrt{2\,\epsilon_j}\; x_{j\sigma\alpha} + \frac{\partial V_o(q_\alpha)}{\partial q}$$

$$+ \frac{\partial E_{o,HF}(\vec{\overline{Q}}_\alpha)}{\partial q} = 0 \tag{63}$$

and

$$\epsilon_j^2\, x_{j\sigma\alpha} + S_{j\sigma}(\vec{\overline{Q}}_\alpha) \sqrt{2\,\epsilon_j} = 0 \quad . \tag{64}$$

If we substitute the equation (64) in equations (62) and (63), we get

$$\omega_\upsilon^2\, q_{\upsilon\alpha} + \frac{\partial E_{o,HF}(\vec{\overline{Q}}_\alpha)}{\partial q_\upsilon}\, C_\upsilon = 0 \tag{65}$$

and

$$\frac{\partial V_o(q_\alpha)}{\partial q} + \frac{\partial E_{o,HF}(\vec{\overline{Q}}_\alpha)}{\partial q} = 0 \tag{66}$$

which are identical with equations (9) and (10). So the extremum of $V(\underline{x}, g, q)$ occurs at the same values of q as the extremum $V(g, q)$. Further, once $\vec{\overline{Q}}_\alpha$ is known, $x_{j\sigma\alpha} = -\sqrt{(2/\epsilon_j)^3}\; S_{j\sigma}(\vec{\overline{Q}}_\alpha)$. Also the value of $V(\underline{x}, g, q)$ at the extremum α is

$$\mathcal{V}_\alpha = V(\underline{x}_\alpha, g_\alpha, q_\alpha)$$

$$= \frac{1}{2} \sum_\upsilon \omega_\upsilon^2 \, q_{\upsilon\alpha}^2 + V_0(q_\alpha) + E_{0,HF}(\vec{\overline{Q}}_\alpha) \qquad (67)$$

$$= V_\alpha \quad . \quad . \qquad (68)$$

The equation (67) is obtained when expressions for $x_{j\sigma\alpha}$, q_α and $q_{\upsilon\alpha}$ are put in the equation (61). The equation (68) implies that the height of the barrier is not changed by the coupling to e-h bosons.

We approximate $V(\underline{x}, g, q)$ in the vicinity of each of its extremum by $\mathcal{V}_\alpha + \delta^2\mathcal{V}_\alpha$ where

$$\mathcal{V}_\alpha = V_0(q_\alpha) + E_{0,HF}(\vec{\overline{Q}}_\alpha) + \frac{1}{2} \omega_\upsilon^2 \, q_{\upsilon\alpha}^2$$

and

$$\delta^2\mathcal{V}_\alpha = \frac{1}{2} \sum_{j,\sigma} \epsilon_j^2 \, \delta x_{j\sigma}^2 + \frac{1}{2} \sum_\upsilon \omega_\upsilon^2 \, \delta q_\upsilon^2 + \sum_{j,\sigma} F_{j\sigma}(\vec{\overline{Q}}_\alpha) \sqrt{2\epsilon_j} \; \delta Q \; \delta x_{j\sigma}$$

$$+ \sum_{j,\sigma} F_{j\sigma}(\vec{\overline{Q}}_\alpha) \sqrt{2\epsilon_j} \; \frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q} \, \delta q \, \delta x_{j\sigma} + Z_\alpha \frac{\delta Q^2}{2} + W_\alpha^2 \frac{\delta q^2}{2}$$

$$+ \left[\frac{1}{2} \frac{\partial^2 E_{0,HF}(\vec{\overline{Q}}_\alpha)}{\partial Q \, \partial q} + 2 \sum_{j,\sigma} \frac{F_{j\sigma}^2(\vec{\overline{Q}}_\alpha)}{\epsilon_j} \frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q} \right] \delta Q \, \delta q \qquad (69)$$

where

$$\delta x_{j\sigma} = x_{j\sigma} - x_{j\sigma\alpha} \ ,$$

$$Z_\alpha = \frac{\partial^2 E_{o,HF}(\vec{\bar{Q}}_\alpha)}{\partial Q^2} + 2 \sum_{j,\sigma} \frac{F^2_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\epsilon_j} \ ,$$

$$W_\alpha^{\ 2} = \frac{\partial^2 E_{o,HF}(\vec{\bar{Q}}_\alpha)}{\partial q^2} + \sum_{j,\sigma} \frac{2F^2_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\epsilon_j} \left[\frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q}\right]^2 + \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} \ ,$$

$$F_{j\sigma}(\vec{\bar{Q}}_\alpha) = \frac{\partial S_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\partial Q} \ ,$$

and

$$\frac{\partial S_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\partial q} = \frac{\partial S_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\partial Q} \frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q} = F_{j\sigma}(\vec{\bar{Q}}_\alpha) \frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q} \ .$$

It is convenient to introduce a new Hamiltonian by

$$H_{na,\alpha} = \frac{1}{2} \left[\sum_{j,\sigma} p_{x_{j\sigma}}^{\ 2} + \sum_{\upsilon} p_\upsilon^{\ 2} + p^2\right] + \mathcal{V}_\alpha + \delta^2\mathcal{V}_\alpha \ . \tag{70}$$

The subscript 'na' stands for non-adiabatic. For $\alpha = 1$ or 3, all the normal modes of the Hamiltonian are stable. For $\alpha = 2$, one mode is unstable. We denote the corresponding frequency by Ω_{na}. Analysing $H_{na,\alpha}$ with $\alpha = 2$ shows that $\Omega_{na,\alpha}$ obeys the equation

$$\Bigg[\left[E''_{o,HF}(\vec{\bar{Q}}_\alpha) - 2\Omega_{na}^2 \int_0^\infty \frac{d\omega_1\ D_\alpha(\omega_1)}{\omega_1(\omega_1^2+\Omega_{na}^2)} \left[1 - \left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)^2}{\partial q}\right)\right]\right] - \Omega_{na}^2$$

$$- \frac{\partial E_{o,HF}(\vec{\bar{Q}}_\alpha)}{\partial Q} \frac{\partial^2\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q^2} - \frac{\partial^2 V_o(q_\alpha)}{\partial q^2}\Bigg] \frac{2}{\pi} \int_0^\infty \frac{d\omega\ \omega\ J(\omega)}{(\omega^2+\Omega_{na}^2)} = 1\ . \tag{71}$$

$D_\alpha(\omega)$ is the "electronic spectral function", defined by[7]

$$D_\alpha(\omega) = \sum_{j,\sigma} \left| F_{j\sigma}(\vec{\bar{Q}}_\alpha) \right|^2 \delta(\omega - \epsilon_j) \tag{72}$$

$$= 2\int_{\varepsilon_F}^{\varepsilon_F+\omega} d\varepsilon\ \rho_a^\sigma(\varepsilon,\ \vec{\bar{Q}}_\alpha)\ \rho_a^\sigma(\varepsilon-\omega,\ \vec{\bar{Q}}_\alpha)\quad . \tag{73}$$

See Appendix C for details. The expression for the rate is

$$\Gamma_{na} = \frac{\Omega_{na}}{2\pi\ \mathrm{Sin}\ (\Omega_{na}/2kT)} \ \frac{\prod_\upsilon \mathrm{Sinh}(\omega_{\upsilon 1}/2kT)}{\prod'_\upsilon \mathrm{Sinh}(\omega_{\upsilon 2}/2kT)} \ \frac{\prod_j \mathrm{Sinh}(\epsilon_{j1}/2kT)}{\prod_j \mathrm{Sinh}(\epsilon_{j2}/2kT)}$$

$$\times \exp(-\Delta V/kT) \tag{74}$$

where $\omega_{\upsilon\alpha}$ and $\epsilon_{j\alpha}$ are the frequencies of the normal modes of $H_{na,\alpha}$. Just as in the adiabatic case,

$$\Gamma_{na} = \frac{\Omega_{na}}{2\pi} \sqrt{|p_o|} \left[\prod_{n=1}^\infty p_n \right] \exp(-\Delta V/kT)\quad . \tag{75}$$

Now p_n is given by

$$p_n = \frac{\prod_{\upsilon}(n^2+Z^2\omega_{\upsilon 1}{}^2)}{(n^2-Z^2\Omega_{na}{}^2)\ \prod_{\upsilon}'(n^2+Z^2\omega_{\upsilon 2}{}^2)}\ \frac{\prod_{j,\sigma}(n^2+Z^2\epsilon_{j1}{}^2)}{\prod_{j,\sigma}(n^2+Z^2\epsilon_{j2}{}^2)} \tag{76}$$

$$= \frac{X_1(n)}{X_2(n)}$$

where

$$X_\alpha(n) = 1 + \left[E''_{o,HF}(\overset{>}{\bar{Q}}_\alpha) + 2n^2Z^{-2}\sum_{j,\sigma}\frac{F^2_{j\sigma}(\overset{>}{\bar{Q}}_\alpha)}{\epsilon_j(n^2Z^{-2}+\epsilon_j{}^2)}\right]\sum_{\upsilon}\frac{C_\upsilon{}^2}{(n^2Z^{-2}+\omega_\upsilon{}^2)}$$

$$+ \left[E''_{o,HF}(\overset{>}{\bar{Q}}_\alpha) + 2n^2Z^{-2}\sum_{j,\sigma}\frac{F^2_{j\sigma}(\overset{>}{\bar{Q}}_\alpha)}{\epsilon_j(n^2Z^{-2}+\epsilon_j^2)}\right]$$

$$\times \frac{\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q}\right)^2}{\left[n^2Z^{-2} + \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial E_{o,HF}(\overset{>}{\bar{Q}}_\alpha)}{\partial Q}\ \frac{\partial^2\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q^2}\right]} \tag{77}$$

(see Appendix C). Using the definitions of $J(\omega)$ and $D_\alpha(\omega)$ the equation (77) can be rewritten as

$$X_\alpha(n) = 1 + \left[E''_{o,HF}(\vec{Q}_\alpha) + 2n^2 Z^{-2} \int_0^\infty \frac{d\omega_1 \; D_\alpha(\omega_1)}{\omega_1(\omega_1^2 + n^2 Z^{-2})} \right] \frac{2}{\pi} \int_0^\infty \frac{d\omega \; \omega \; J(\omega)}{(\omega^2 + n^2 Z^{-2})}$$

$$+ \left[E''_{o,HF}(\vec{Q}_\alpha) + 2n^2 Z^{-2} \int_0^\infty \frac{d\omega_1 \; D_\alpha(\omega_1)}{\omega_1(\omega_1^2 + n^2 Z^{-2})} \right]$$

$$\times \frac{\left[\frac{\partial \varepsilon_{a\sigma}(Q_\alpha, \; q_\alpha)}{\partial q} \right]^2}{\left[n^2 \; Z^{-2} + \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial E_{o,HF} \; (\vec{Q}_\alpha)}{\partial Q} \; \frac{\partial^2 \varepsilon_{a\sigma}(Q_\alpha, \; q_\alpha)}{\partial q^2} \right]} \quad . \qquad (78)$$

Thus to calculate $X_\alpha(n)$ one has to know $D_\alpha(\omega)$. An approximation to $D_\alpha(\omega)$ can be written as

$$D_\alpha(\omega) = 2 \int_{\varepsilon_F}^{\varepsilon_F + \omega} d\varepsilon \; \rho_a^\sigma(\varepsilon, \; \vec{Q}_\alpha) \; \rho_a^\sigma(\varepsilon - \omega, \; \vec{Q}_\alpha)$$

$$= \omega \;\; \rho_a^\sigma(\varepsilon_F, \; \vec{Q}_\alpha) \; \left[\rho_a^\sigma(\varepsilon_F - \omega, \; \vec{Q}_\alpha) + \rho_a^\sigma(\varepsilon_F + \omega, \; \vec{Q}_\alpha) \right] \qquad (79)$$

(see Appendix C). This the trapezoidal approximation to the integral. Using this approximation $D_\alpha(\omega)$ and Drude form of $J(\omega)$, $X_\alpha(n)$ can be evaluated as

$$X_\alpha(n) = 1 + \frac{4E_r Z\,\omega_D}{(n+Z\omega_D)} \quad \rho_a^\sigma(\varepsilon_F,\ \vec{\overline{Q}}_\alpha)\left[-1+\frac{n(n+Z\Delta)}{(n+Z\Delta)^2+Z^2\left[\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)+\varepsilon_F\right]^2}\right]$$

$$+ \frac{2\left[\dfrac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q}\right]^2 \rho_a^\sigma(\varepsilon_F,\ \vec{\overline{Q}}_\alpha)}{\left[n^2 Z^{-2} + \dfrac{\partial^2 V_0(q_\alpha)}{\partial q^2} + \dfrac{\partial E_{0,HF}(\vec{\overline{Q}}_\alpha)}{\partial Q}\ \dfrac{\partial^2\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q^2}\right]}$$

$$\times \left[-1 + \frac{n(n+Z\Delta)}{(n+Z\Delta)^2 + Z^2\left[\varepsilon_{a\sigma}(Q_\alpha, q_\alpha)-\varepsilon_F\right]^2}\right] \tag{80}$$

$$= 1 + \left[\frac{4E_r Z\omega_D\ \rho_a^\sigma(\varepsilon_F,\ \vec{\overline{Q}}_\alpha)}{(n\ +\ Z\omega_D)} + \frac{2\left[\dfrac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q}\right]^2 \rho_a^\sigma(\varepsilon_F,\ \vec{\overline{Q}}_\alpha)Z^2}{(n\ +\ Z^2\ \bar{V}_\alpha{}^2)}\right]$$

$$\times \left[\frac{-\ Z\Delta(n+Z\Delta)\ +\ Z^2\ (\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)\ -\ \varepsilon_F)^2}{(n+Z\Delta)^2\ +\ Z^2\ (\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)\ -\ \varepsilon_F)^2}\right] \tag{81}$$

where

$$\bar{V}_\alpha^2 = \frac{\partial^2 V_0(q_\alpha)}{\partial q^2} + \frac{\partial E_0(\vec{\bar{Q}}_\alpha)}{\partial Q^2} \; \frac{\partial^2 \varepsilon_{a\sigma}(Q_\alpha \, , \, q_\alpha)}{\partial q^2} \quad .$$

$$X_\alpha(n) =$$

$$\frac{\begin{array}{l}(n+Z\omega_D)(n^2+Z^2\bar{V}_\alpha^2)\Big[(n+Z\Delta)^2+Z^2(\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)\ -\varepsilon_F)^2\Big] \ -4E_r Z\omega_D \rho_a^\sigma(\varepsilon_F,\vec{\bar{Q}}_\alpha) \\ \times\ (n^2+Z^2\bar{V}_\alpha{}^2)\Big(Z\Delta(n+Z\Delta)\Big) \ + \ Z^2(\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)-\varepsilon_F)^2 \ - \ 2Z^2\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q}\right)^2 \\ \times\ \rho_a^\sigma(\varepsilon_F,\vec{\bar{Q}}_\alpha)(n+Z\Delta) \ \Big[Z\Delta(n+z\Delta)+Z^2(\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)\ -\varepsilon_F)^2\ \Big]\end{array}}{(n+Z\Delta)(n^2+Z^2\bar{V}_\alpha^2)\Big[(n+Z\Delta)^2+\ Z^2\ \big(\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)-\varepsilon_F\big)^2\ \Big)}$$

(82)

Then the expression for the rate becomes

$$\Gamma_{na} = \frac{\Omega_{na}}{2\pi} \sqrt{\frac{1 \ - \ 2E_r E''_{o,HF}(\vec{\bar{Q}}_1) \ - \ \left(\frac{\partial\varepsilon_{a\sigma}(Q_1,\ q_1)}{\partial q}\right)^2 \ E''_{o,HF}(\vec{\bar{Q}}_1)\ \bar{V}_1{}^2}{1 \ - \ 2E_r E''_{o,HF}\ (\vec{\bar{Q}}_2) \ - \ \left(\frac{\partial\varepsilon_{a\sigma}(Q_2,\ q_2)}{\partial q}\right)^2 \ E''_{o,HF}(\vec{\bar{Q}}_2)\ \bar{V}_2{}^2}}$$

$$\times \left(\prod_{n=1}^{\infty} \frac{A_2(n)}{A_1(n)} \right) \left(\prod_{m=1}^{\infty} \frac{S_2(m)}{S_1(m)} \right) \left(\prod_{l=1}^{\infty} \frac{Y_1(l)}{Y_2(l)} \right) \exp(-\Delta V/kT) \qquad (83)$$

where $A_\alpha(n)$, $S_\alpha(m)$ and $Y_\alpha(l)$ are given by

$$A_\alpha(n) \ = \ n^2 \ + \ Z^2 \ \bar{V}_\alpha{}^2 \qquad (84)$$

$$S_\alpha(m) \ = \ (m+Z\Delta)^2 \ + \ Z^2(\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)-\ \varepsilon_F)^2 \qquad (85)$$

and

$$- 4E_r Z\omega_D \rho_a^{\sigma}(\varepsilon_F,\ \bar{Q}_{\alpha}^{>})\ \left[Z\Delta(1+Z\Delta)+Z^2\left(\varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})-\ \varepsilon_F\right)^2\right]\ \left(1^2+Z^2\bar{V}_{\alpha}^2\right)$$

$$- 2Z^2\left[\frac{\partial\varepsilon_{a\sigma}(Q_{\alpha},q_{\alpha})}{\partial q}\right]^2 \rho_a^{\sigma}(\varepsilon_F,\ \bar{Q}_{\alpha}^{>})\left[Z\Delta(1+Z\Delta)+Z^2\left(\varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})-\varepsilon_F\right)^2\right]\left(1+Z\omega_D\right). \tag{86}$$

Each of the infinite products in equation (83) may be expressed in terms of Gamma Functions. Thus we obtain

$$\Gamma_{na} = \frac{\Omega_{na}}{2\pi}\sqrt{\frac{1\ -\ 2E_r E''_{o,HF}(\bar{Q}_1^{>})\ -\ \left[\frac{\partial\varepsilon_{a\sigma}(Q_1,\ q_1)}{\partial q}\right]^2 E''_{o,HF}(\bar{Q}_1^{>})\ \bar{V}_1^2}{1\ -\ 2E_r E''_{o,HF}(\bar{Q}_2^{>})\ -\ \left[\frac{\partial\varepsilon_{a\sigma}(Q_2,\ q_2)}{\partial q}\right]^2 E''_{o,HF}(\bar{Q}_2^{>})\ \bar{V}_2^2}}$$

$$\times\ \frac{\Gamma\left(1-iZ\bar{V}_1\right)\ \ \Gamma\left(1+iZ\bar{V}_1\right)\ \ \Gamma\left(1-Z\Delta-iZ(\varepsilon_{a\sigma}(Q_1,\ q_1)\ -\varepsilon_F)\right)}{\Gamma\left(1-iZ\bar{V}_2\right)\ \ \Gamma\left(1+iZ\bar{V}_2\right)\ \ \Gamma\left(1-Z\Delta-iZ(\varepsilon_{a\sigma}(Q_2,\ q_2)\ -\varepsilon_F)\right)}$$

$$\times\ \frac{\Gamma\left(1-Z\Delta+iZ(\varepsilon_{a\sigma}(Q_1,\ q_1)\ -\varepsilon_F)\right)}{\Gamma\left(1-Z\Delta+iZ(\varepsilon_{a\sigma}(Q_2,\ q_2)\ -\varepsilon_F)\right)}\ \prod_{i=1}^{5}\ \frac{\Gamma\left(1-Z\Lambda_{i,2}\right)}{\Gamma\left(1-Z\Lambda_{i,1}\right)}\quad \exp(-\Delta V/kT)\ . \tag{87}$$

$\Lambda_{i,\alpha}$ are the roots of the equation $Y_{\alpha}(Z\Lambda)\ =\ 0$. This equation, written out explicitly, is

$$\left[\left(\Lambda+\Delta\right)^2\ +\ \left(\varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})-\ \varepsilon_F\right)^2\right]\ \left(\Lambda^2+\bar{V}_{\alpha}^{\ 2}\right)\left(\Lambda+\omega_D\right)\ -\ 4E_r Z\omega_D\rho_a^{\sigma}(\varepsilon_F,\ \bar{Q}_{\alpha}^{>})$$

$$\times\ \left[\Delta\left(\Lambda+\Delta\right)+\left(\varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})\ -\varepsilon_F\right)^2\right]\left(\Lambda^2+\bar{V}_{\alpha}^{\ 2}\right)\ -\ 2\left[\frac{\partial\varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})}{\partial q}\right]^2\rho_a^{\sigma}(\varepsilon_F,\ \bar{Q}_{\alpha}^{>})$$

$$\times\ \left[\Delta\left(\Lambda+\Delta\right)+\left(\varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})\ -\varepsilon_F\right)^2\right]\left(\Lambda+\omega_D\right)\ \ =\ \ 0\ \ . \tag{88}$$

This is a polynomial equation in $\wedge$ of order five and its roots can be found out numerically. Thus the equation (87) is the final rate expression for the proton transfer reaction, taking into account of non-adiabaticity.

(8) EVALUATION OF DIFFERENT TERMS IN THE RATE EXPRESSIONS [EQUATIONS (40) AND (83)]

In the following, we discuss briefly how simple minded calculations may be done using the above formulae. Calculations need knowledge of the electronic energy, $E_{o,HF}(Q, q)$. This requires the density of states function, $\Delta(\varepsilon, q)$. A suitable form for this is a semielliptical one[13]. As the H^+ is in vicinity of the metal atom, there would usually be a metal orbital interacting most strongly with it. Let us denote it by $|M\rangle$. $|M\rangle$, could, for example a $3d_z^2$ orbital on the Nickel (Ni) atom, for hydrogen discharge on the surface of Ni. This orbital would form a band of width `4β' due to its interaction with neighbouring orbitals. We take the band to extent from (-2β) to $(+2\beta)$. It is usual in chemisorption theory[11,12], to adopt (equation (21))

$$\Delta(\varepsilon, q) = \pi \sum_k |V_{ak}(q)|^2 \, \delta(\varepsilon - \varepsilon_k)$$

$$= \frac{2\,\beta'^2(q)}{2\beta} \sqrt{4\beta^2(q) - \varepsilon^2} \qquad (89)$$

$\beta'(q)$ is the hopping integral between $|a\rangle$ and $|M\rangle$, defined by

$$\beta'(q) = \langle a|H|M\rangle \quad . \tag{90}$$

A semi-empirical evaluation of $\beta'(q)$ would lead to[15]

$$\beta'(q) = \left[\langle a|H|a\rangle + \langle M|H|M\rangle\right] \langle M|a\rangle \tag{91}$$

where $\langle M|a\rangle$ is the overlap integral and, hence is q dependent.

Using this semielliptical form for $\Delta(\varepsilon, q)$ and following Newns[13], adopting a system of units in which energy is measured in units of 2β, the occupation number of $|a\uparrow\rangle$, may be found to be

$$\langle n_{a\uparrow}\rangle = \frac{1}{\pi}\int_{-1}^{\varepsilon_F} d\varepsilon\, \rho_a^{\sigma}(\varepsilon, Q, q) \quad . \tag{92}$$

From the equation (24), we get

$$\langle n_{a\uparrow}\rangle = \frac{1}{\pi}\int_{-1}^{\varepsilon_F} d\varepsilon \frac{\Delta(\varepsilon, q)}{\pi\left[(\varepsilon-\varepsilon_{a\sigma}(Q, q)-\Pi(\varepsilon, q))\right]^2 + \Delta^2(\varepsilon, q)} \quad . \tag{93}$$

Note that we are making use of the restricted Hartree-Fock approximation so that $\langle n_{a\uparrow}\rangle = \langle n_{a\downarrow}\rangle$. The above equation may be integrated to give

$$\langle n_{a\uparrow}\rangle = 2\pi^{-1}\left[\beta'(q)\right]^2\left[\left[1-\frac{1}{R-R_c}\left[\frac{1}{(R^2-1)^{1/2}}-\frac{1}{(R_c^2-1)^{1/2}}\right]\right]\right]$$

$$\times\left[\mathrm{ArcSin}(\varepsilon_F)+\frac{\pi}{2}\right] \qquad (94)$$

where

$$R = \left[1-4\beta'^2(q)\right]^{-1}\left[\left(1-2\beta'^2(q)\right)\varepsilon_{a\sigma}(Q,\ q)+2i\beta'^2(q)\left(1-4\beta'^2(q)\right.\right.$$

$$\left.\left. -\ \varepsilon_{a\sigma}^2(Q,\ q)\right)^{1/2}\right]$$

and R_c is the complex conjugate of R. The bracket in the $\langle n_{a\uparrow}\rangle$ indicates taking expectation values with respect to the ground state, which may be iteratively solved on a computer, to obtain self consistent values of $\langle n_{a\uparrow}\rangle$ for any $\varepsilon_a(q)$ and U(q).

The above expression for the occupation number (equation (94)) has been obtained assuming the absence of localised states. When a localised state exists below the band , we have to add a term $\langle n_{a\uparrow}\rangle_l$ to the equation (92), $\langle n_{a\uparrow}\rangle_l$ being the occupation number of a localised state, which is obtained in the semielliptical approximation[13] as $(1-4\beta'^2(q)^{-1}\left[(1-2\beta'^2(q)) + 2\beta'^2(q)\varepsilon_{a\sigma}(Q,\ q)\left(4\beta'^2(q)+\varepsilon_{a\sigma}^2(Q,\ q)\ \ -1\right)^{-1/2}\right]$, and the equations will get modified correspondingly.

From equation (94), it is clear that $\langle n_{a\uparrow}\rangle$, the occupation number of the orbital $|a\uparrow\rangle$ depends on the position of the Fermi level, ε_F. The overpotential, η measures the deviation of ε_F from its equilibrium value. So $\langle n_{a\uparrow}\rangle$ is dependent on η. Since the rate depends on the electronic energy, $E_{o,HF}(Q, q)$ which in turn depends on $\langle n_{a\uparrow}\rangle$, the rate of the proton transfer reaction will depend on η. The η dependence of the rate can be calculated.

(8.a) Estimation of $\varepsilon_a(q)$ and U(q)

An analytical expression for the dependence of ε_a on q is (see Appendix A)

$$\varepsilon_a(q) = -I+L(q +R(q)-eV_{H^+}(q) \qquad (95)$$

where

I = Ionization potential of proton, equal to 313.6 kcals.

L(q) is the hydration energy, which is taken as theMorse molecular potential[16,17],

$$L(q) = L_o\left[2ex\ \left(-a(q_e-q)\right)-\exp\left(-2a(q_e-q)\right)\right] \text{ kcals mole}^{-1} \qquad (96)$$

where L_o is the hydration energy at $q = q_e$, equal to 275.79 kcals mole^{-1} and q_e is the equilibrium distance of H from the metal surface, q and q_e measured in Å, a is a quantity, measured in $(Å)^{-1}$, related to the force constant k of the bond H^+-H_2O and the reduced mass μ of the system

$$a = \frac{1}{2\pi}\sqrt{\frac{k}{2\mu}}$$

R(q) is the H-H_2O repulsive potential energy, which is taken as exponential core repulsion and written as[16,17]

$$R(q) = 14.4 \left[56.7 \exp\left(-24.9(\delta-q)^2\right)+21.5(\delta-q)\exp\left(-2.4(\delta-q)^2\right)\right] \quad (97)$$
$$\text{kcals mole}^{-1}$$

δ is the distance of closest approach of water molecules to the metal surface, which is taken to be 3.77Å.

$V_{H^+}(q)$ is the electrostatic potential at H^+ which depends on q as

$$eV_{H^+}(q) = \frac{-e^2}{4q} \quad . \qquad (98)$$

Due to image interaction, U is shown to have a functional dependence on the position with respect to the metal surface[18], as $U(q) = U_o - e^2/2q$, where U_o is the asymptotic value, equal to U_o = 297.47 kcals.

Our Hamiltonian (equation (2)) describes only the valence electrons. But, inorder to calculate the total electronic energy, we have to add the core-core (hydrogen-metal atom) repulsion energy, $V_o(q)$, to the electronic energy, $E_{o,HF}(Q, q)$ calculated from the above Hamiltonian . The nuclear repulsion between ith atom in the solid and the hydrogen atom, V_{Hi} may be taken as[18]

$$V_{Hi} = \frac{Ze^2}{q_{Hi}} \exp(-aq_{Hi}) \qquad (99)$$

where q_{Hi} is the H distance from the atom i of the metal, Z is valence charge per atom and e is the electronic charge. The equation (99) is the Thomas-Fermi screened coulomb interaction and 'a' is the corresponding screening constant.

To get the total repulsion energy, the sum of V_{Hi} is taken on the atom i of the crystal. Such a sum is performed on the metal lattice near the adatom, by increasing the number of sites until good convergence is obtained. Thus

$$V_0(q) = \sum_i V_{Hi} \tag{100}$$

The so obtained total energy will have all the electronic and nuclear contributions. Thus the quantities in our rate expression for electrochemical proton transfer reaction can be calculated easily.

APPENDIX A. Expression for $\varepsilon_a(q)$

An explicit expression for $\varepsilon_a(q)$, the original energy of $|a\rangle$ on the H_3O^+ ion, is found as follows. ε_a is the difference in the energies between two states, defined below. (1) The state $M\text{-}H^+\text{-}OH_2$ and (2) A state with electron occupying the orbital of H_3O^+ so that the species is $M\text{-}H\text{-}OH_2$. The energy of state (1) is $-L(q) + eV_{H^+}(q)$, where $L(q)$ is the hydration energy which is taken as Morse molecular potential, the explicit expression for which is given in the text (see equation (96)) and $eV_{H^+}(q)$ is the electrostatic potential at H^+ ion (see equation (98)), while that of state (2) is given by $-I + R(q)$, where I is the ionisation potential of proton and R(q) is H-H_2O repulsion energy which is taken as exponential core repulsion and the expression for this is given in the text (see equation (97)). Then the expression for $\varepsilon_a(q)$ becomes, energy of state(2) - energy of state(1) = $-I+R(q)+L(q)-eV_H+(q)$, which is the expression used in the text (see equation (95)).

APPENDIX B. ADIABATIC CASE

(1) Normal mode analysis

We wish to determine the frequencies of the normal modes of H_α given in equation (28). Writing the classical equations of motion for δq_υ gives

$$\frac{d^2\delta q_\upsilon}{dt^2} = \ddot{\delta q_\upsilon} = -\omega_\upsilon{}^2\delta q_\upsilon - \left(\frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial Q\ \ \partial q}\right) C_\upsilon \delta q\ - \left(\frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial Q^2}\right) C_\upsilon \delta Q \tag{B.1}$$

and

$$\frac{d^2\delta q}{dt^2} = \ddot{\delta q} = \left(-\frac{\partial^2 V_o(q_\alpha)}{\partial q^2} - \frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial q^2}\right)\delta q - \left(\frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial Q\ \partial q}\right)\delta Q \tag{B.2}$$

Now we put $\delta q_\upsilon = \delta q_\upsilon{}^o e^{i\omega t}$ and $\delta q = \delta q^o e^{i\omega t}$, where ω is the frequency of a normal mode of H_α and $\delta q_\upsilon{}^o$ and δq^o are independent of t. Substitution of these expressions for δq_υ and δq in equations (B.1) and (B.2) leads to the following equations.

$$\delta q_{\upsilon}^{0} = -\sum_{\upsilon} \frac{C_{\upsilon}^{2}}{(\omega_{\upsilon}^{2}-\omega^{2})}\left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q\, \partial q}\right]\delta q^{0} - \sum_{\upsilon}\frac{C_{\upsilon}^{2}}{(\omega_{\upsilon}^{2}-\omega^{2})}\left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q^{2}}\right] \times \delta q_{\upsilon}^{0} \qquad \text{(B.3)}$$

Substituting this equation in $\delta Q^{0} = \sum_{\upsilon} C_{\upsilon}\delta q_{\upsilon}^{0}$ and rearranging the resultant equation leads

$$\left[1+\sum_{\upsilon} \frac{C_{\upsilon}^{2}}{(\omega_{\upsilon}^{2}-\omega^{2})}\left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q^{2}}\right]\right]\delta Q^{0} = \left[-\left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q\, \partial q}\right]\sum_{\upsilon}\frac{C_{\upsilon}^{2}}{(\omega_{\upsilon}^{2}-\omega^{2})}\right]\delta q^{0} \qquad \text{(B.4)}$$

and the equation for δq^{0} becomes

$$\delta q^{0} = \frac{-\left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q\, \partial q}\right]\delta Q^{0}}{\left[-\omega^{2} + \frac{\partial^{2} V_{0}(q_{\alpha})}{\partial q^{2}} + \frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial q^{2}}\right]} . \qquad \text{(B.5)}$$

Substituting the equation (B.5) in equation (B.4), we get

$$\sum_{\upsilon} \frac{C_{\upsilon}^{2}}{(\omega_{\upsilon}^{2}-\omega^{2})}\left[\frac{\left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q\, \partial q}\right]^{2}}{\left[-\omega^{2} + \frac{\partial^{2} V_{0}(q_{\alpha})}{\partial q^{2}} + \frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial q^{2}}\right]} - \left[\frac{\partial^{2} E_{o,HF}(Q_{\alpha}, q_{\alpha})}{\partial Q^{2}}\right]\right] \qquad \text{(B.6)}$$

$$= 1 .$$

Using the definition of $J(\omega)$ in equation (B.6), this becomes

$$\frac{2}{\pi}\int_0^\infty \frac{\omega J(\omega)\,d\omega}{(\omega_\upsilon^2-\omega^2)}\left[\frac{\left(\frac{\partial^2 E_{o,HF}(Q_\alpha,\, q_\alpha)}{\partial Q\,\partial q}\right)^2}{\left(-\omega^2+\frac{\partial^2 V_o(q_\alpha)}{\partial q^2}+\frac{\partial^2 E_{o,HF}(Q_\alpha,\, q_\alpha)}{\partial q^2}\right)} - \left(\frac{\partial^2 E_{o,HF}(Q_\alpha,\, q_\alpha)}{\partial Q^2}\right)\right]$$

$$= 1 . \tag{B.7}$$

Of special interest to us is the unstable mode, whose frequency ω is purely imajinary, which exists for $\alpha = 2$. Putting $\omega^2 = -\Omega_a^2$ into equation (B.7) gives equation (29) of the text.

(2) Evaluation of p_n

The definition of p_n in equation (35) may be written as

$$p_n = \frac{\prod_\upsilon (n^2+Z^2\omega_{\upsilon 1}^2)}{\prod_\upsilon (n^2+Z^2\omega_{\upsilon 2}^2)}$$

(remember $\omega^2 = -\Omega^2$). So

$$\ln p_n = \sum_\upsilon \ln(n^2+Z^2\omega_{\upsilon 1}^2) - \sum_\upsilon \ln(n^2+Z^2\omega_{\upsilon 2}^2) . \tag{B.8}$$

As $\omega_{\upsilon\alpha}^2$ are the eigen values of $(G^{(\alpha)})$,

where

$$G^{(\alpha)} = G_o + G_1 . \tag{B.9}$$

$$\ln p_n = \mathrm{Tr}\ \ln(n^2 I + Z^2 G^{(1)}) - \mathrm{Tr}\ \ln(n^2 I + Z^2 G^{(2)})$$

$$= \mathrm{Tr}\ \ln(n^2 I + Z^2 (G_o + G_1^{(1)})) - \mathrm{Tr}\ \ln(n^2 I + Z^2 (G_o + G_1^{(2)})) \tag{B.10}$$

I is the NxN matrix. Tr stands for trace. We define matrices G and $G^{(\alpha)}$ by

$$G_o = \begin{bmatrix} \omega_\upsilon^{\ 2} \delta_{\upsilon\upsilon_1} & 0 \\ 0 & \dfrac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \dfrac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial q^2} - \dfrac{B^2(Q_\alpha,\ q_\alpha)}{E''_{o,HF}(Q_\alpha,\ q_\alpha)} \end{bmatrix} \tag{B.11}$$

and

$$G_1^{(\alpha)} = E''_{o,HF}(Q_\alpha,\ q_\alpha\ ) \begin{bmatrix} C_\upsilon C_\upsilon' & \dfrac{B(Q_\alpha,\ q_\alpha)}{E''_{o,HF}(Q_\alpha,\ q_\alpha)} C_\upsilon \\ \dfrac{B(Q_\alpha,\ q_\alpha)}{E''_{o,HF}(Q_\alpha,\ q_\alpha)} C_\upsilon & \left[\dfrac{B(Q_\alpha,\ q_\alpha)}{E''_{o,HF}(Q_\alpha,\ q_\alpha)}\right]^2 \end{bmatrix} \tag{B.12}$$

which can be written ia simpler form

$G_o = \omega_\upsilon^{\ 2} \delta_{\upsilon\upsilon_1}$, $\upsilon = 1,2\ 3,\ldots\ldots\ldots N+1$, where

$$\omega_{N+1}^{\ 2} = \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} + \frac{\partial^2 E_{o,HF}(Q_\alpha,\ q_\alpha)}{\partial q^2} - \frac{B^2(Q_\alpha,\ q_\alpha)}{E''_{o,HF}(Q_\alpha,\ q_\alpha)} \tag{B.13}$$

and

$$G_1^{(\alpha)} = E''_{o,HF}(Q_\alpha, q_\alpha)\, A_\upsilon\, A_\upsilon' \,, \quad \upsilon = 1,2,3,\ldots\, N+1 \qquad (B.14)$$

where

$$A_\upsilon = \begin{bmatrix} A_1 \\ A_2 \\ \cdot \\ A_{N+1} \end{bmatrix} \quad ; \quad A_\upsilon' = \begin{bmatrix} A_1, & A_2, \ldots & A_{N+1} \end{bmatrix}$$

$$A_{N+1} = \frac{B(Q_\alpha, q_\alpha)}{E''_{o,HF}(Q_\alpha, q_\alpha)} \quad \text{and} \quad B(Q_\alpha, q_\alpha) = \frac{\partial^2 E_{o,HF}(Q_\alpha, q_\alpha)}{\partial Q\, \partial q} \; .$$

Then

$$\ln p_n = \mathrm{Tr}\, \ln(1+y^{-1}Z^2G_1^{(1)}) - \mathrm{Tr}\, \ln(1+y^{-1}Z^2G_1^{(2)}) \qquad (B.15)$$

$y = n^2 I + Z^2 G_0$ is a diagonal matrix. Expanding the logarithmic function, we get

$$\mathrm{Tr}\ \ln(1+y^{-1}Z^2G_1^{(\alpha)}) = \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m} Z^{2m}\ \mathrm{Tr}(y^{-1}G_1^{(\alpha)})^m . \qquad (B.16)$$

But

$$\mathrm{Tr}(y^{-1}G_1^{(\alpha)})^m = \left[\sum_{\upsilon=1}^{N+1} (n^2+Z^2\omega_\upsilon{}^2)^{-1}\ E''_{o,HF}(Q_\alpha,\ q_\alpha)\ A_\upsilon^2\right] \qquad (B.17)$$

as can be easily seen from the definitions of y, G_0 and $G_1{}^{(\alpha)}$ above. Equations (B.16) and (B.17) give

$$\mathrm{Tr}\ \ln(1+y^{-1}Z^2G_1^{(\alpha)}) = \ln\left[1 + \sum_{\upsilon=1}^{N+1} (n^2+Z^2\omega_\upsilon^2)^{-1} Z^2E''_{o,HF}(Q_\alpha,\ q_\alpha)A_\upsilon{}^2\right]$$

$$(B.18)$$

Using this in equation (B.15), and taking the exponentials, we obtain

$$p_n = \frac{1 + \sum_{\upsilon=1}^{N+1} (n^2+Z^2\omega_\upsilon{}^2)^{-1}\ Z^2\ E''_{o,HF}(Q_1,\ q_1)\ A_\upsilon^2}{1 + \sum_{\upsilon=1}^{N+1} (n^2+Z^2\omega_\upsilon{}^2)^{-1}\ Z^2\ E''_{o,HF}(Q_2,\ q_2)\ A_\upsilon^2} =$$

$$\frac{1+(n^2+Z^2\omega_1{}^2)^{-1}Z^2E''_{o,HF}(Q_1,\ q_1)A_1^2 + ..(n^2+Z^2\omega_{N+1}^2)^{-1}Z^2E''_{o,HF}(Q_1,q_1)A_{N+1}^2}{1+(n^2+Z^2\omega_2{}^2)^{-1}Z^2E''_{o,HF}(Q_2,\ q_2)A_2^2 + ..(n^2+Z^2\omega_{N+1}^2)^{-1}Z^2E''_{o,HF}(Q_2,q_2)A_{N+1}^2}$$

$$= \frac{1+\sum_{\upsilon=1}^{N}(n^2+Z^2\omega_\upsilon^2)^{-1}Z^2E''_{o,HF}(Q_1,\ q_1)A_\upsilon^2 + (n^2+Z^2\omega_{N+1}^2)^{-1}Z^2E''_{o,HF}(Q_1,\ q_1)A_{N+1}^2}{1+\sum_{\upsilon=1}^{N}(n^2+Z^2\omega_\upsilon^2)^{-1}Z^2E''_{o,HF}(Q_2,\ q_2)A_\upsilon^2 + (n^2+Z^2\omega_{N+1}^2)^{-1}Z^2E''_{o,HF}(Q_2,\ q_2)A_{N+1}^2}$$

$$= \frac{X_1(n)}{X_2(n)} \tag{B.19}$$

where $X_\alpha(n)$ is given by

$$X_\alpha(n) = 1 + \sum_{\upsilon=1}^{N} (n^2+Z^2\omega_\upsilon^2)^{-1} Z^2 \; E''_{o,HF}(Q_\alpha, q_\alpha) A_\upsilon^2$$

$$+ \; (n^2+Z^2\omega_{N+1}^2)^{-1} Z^2 \; E''_{o,HF}(Q_2, q_2) \; A_{N+1}^2 \tag{B.20}$$

Using the definition of $J(\omega)$ in equation (B.20), we get equation (36) in the text.

APPENDIX C. NON-ADIABATIC CASE

(1) Normal mode analysis

The Hamiltonian $H_{na,\alpha}$ leads to the following classical equations of motion.

$$\delta\ddot{q}_\upsilon = -\omega_\upsilon^2\,\delta q_\upsilon - \sum_{j,\sigma} F_{j\sigma}(\vec{\bar{Q}}_\alpha)\sqrt{2\,\epsilon_j}\;C_\upsilon\delta x_{j\sigma} - Z_\alpha C_\upsilon \delta Q - \left[\frac{1}{2}\,\frac{\partial^2 E_{o,HF}(\vec{\bar{Q}}_\alpha)}{\partial Q\;\partial q} + \sum_{j,\sigma}\frac{2F^2_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\epsilon_j}\;\frac{\partial \varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\right]C_\upsilon\;\delta q \tag{C.1}$$

$$\delta\ddot{q} = \sum_{j,\sigma} F_{j\sigma}(\vec{\bar{Q}}_\alpha)\;\sqrt{2\,\epsilon_j}\;\frac{\partial \varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\,\delta x_{j\sigma} - W_\alpha^{\,2}\delta q - \left[\frac{1}{2}\,\frac{\partial^2 E_{o,HF}(\vec{\bar{Q}}_\alpha)}{\partial Q\;\partial q} + \sum_{j,\sigma}\frac{2F^2_{j\sigma}(\vec{\bar{Q}}_\alpha)}{\varepsilon_j}\;\frac{\partial \varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\right]\delta Q \tag{C.2}$$

$$\delta\ddot{x}_{j\sigma} = -\epsilon_j^2\;\delta x_{j\sigma} - F_{j\sigma}(\vec{\bar{Q}}_\alpha)\;\sqrt{2\,\epsilon_j}\;\delta Q - F_{j\sigma}(\vec{\bar{Q}}_\alpha)\;\sqrt{2\,\epsilon_j}\;\left(\frac{\partial \varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\right)\delta q \tag{C.3}$$

Putting $\delta q_\upsilon = \delta q_\upsilon^{\,o} e^{i\omega t}$; $\delta q = \delta q^o e^{i\omega t}$ and $\delta x_j^{\,o} e^{i\omega t}$, where ω is the frequency of a normal mode of $H_{na,\alpha}$, we get

$$\omega^2\,\delta q_\upsilon^0 = \sum_{j,\sigma} F_{j\sigma}(\vec{\overline{Q}}_\alpha)\sqrt{2\,\epsilon_j}\;C_\upsilon\,\delta x_{j\sigma}^0 + \omega_\upsilon^2\,\delta q_\upsilon^0 + Z_\alpha\,C_\upsilon C_\upsilon\,\delta q_\upsilon^0$$

$$+\left[\frac{1}{2}\,\frac{\partial^2 E_{o,HF}(\vec{\overline{Q}}_\alpha)}{\partial Q\,\partial q} + \sum_{j,\sigma}\frac{F_{j\sigma}^2(\vec{\overline{Q}}_\alpha)}{\epsilon_j}\,\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\right] C_\upsilon\,\delta q^0 \qquad (C.4)$$

$$\omega^2\delta q^0 = \sum_{j,\sigma} F_{j\sigma}(\vec{\overline{Q}}_\alpha)\sqrt{2\,\epsilon_j}\;\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\,\delta x_{j\sigma}^0 + W_\alpha^2\delta q^0 + \left[\frac{1}{2}\,\frac{\partial^2 E_{o,HF}(\vec{\overline{Q}}_\alpha)}{\partial Q\,\partial q}\right.$$

$$\left.+\sum_{j,\sigma}\frac{2F_{j\sigma}^2(\vec{\overline{Q}}_\alpha)}{\epsilon_j}\,\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\right] C_\upsilon\,\delta q_\upsilon^0 \qquad (C.5)$$

$$\omega^2\delta x_{j\sigma}^0 = F_{j\sigma}(\vec{\overline{Q}}_\alpha)\sqrt{2\,\epsilon_j}\;C_\upsilon\,\delta q_\upsilon^0 + \epsilon_j^2\,\delta x_{j\sigma}^0 + F_{j\sigma}(\vec{\overline{Q}}_\alpha)\sqrt{2\,\epsilon_j}$$

$$\times\,\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\,\delta q^0 \qquad (C.6)$$

Solving for $\delta x_{j\sigma}^0$ from equation (C.6), substituting it in equation (C.5) for δq^0 and substituting this in equation (C.4) and finally solving for δq_υ^0 from the resultant equation, we get

$$\delta q_\upsilon^0 = \frac{C_\upsilon\,\delta Q^0}{(\omega^2-\omega_\upsilon^2)}\left[Z_\alpha + \sum_{j,\sigma}\frac{2F_{j\sigma}^2(\vec{\overline{Q}}_\alpha)\,\epsilon_j}{(\omega^2-\epsilon_j^2)} + K(\vec{\overline{Q}}_\alpha,\,\omega,\,\epsilon_j)\right] \qquad (C.7)$$

where

$$K(\vec{\overline{Q}}_\alpha,\,\omega,\,\epsilon_j) = \omega^2 - W_\alpha^2 - \sum_{j,\sigma}\frac{2F_{j\sigma}^2(\vec{\overline{Q}}_\alpha)\,\epsilon_j}{(\omega^2-\epsilon_j^2)}\left[\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\,q_\alpha)}{\partial q}\right]^2 .$$

Substituting for W_α^2 in equation (C.7), we get

$$\delta q_\upsilon{}^{o} = \frac{C_\upsilon\ \delta Q^{o}}{(\omega^2-\omega_\upsilon{}^2)} \left[\left[Z_\alpha + \sum_{j,\sigma} \frac{2F_{j\sigma}^2(\vec{Q}_\alpha)\ \epsilon_j}{(\omega^2-\epsilon_j{}^2)} \right] \left[1 - \left[\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q} \right] \right. \right.$$

$$\left. - \frac{\partial E_{o,HF}(\vec{Q}_\alpha)}{\partial Q}\ \frac{\partial^2\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q^2}\ \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} \right] \quad . \tag{C.8}$$

Substituting this equation in $\sum_\upsilon C_\upsilon \delta q_\upsilon{}^{o} = \delta Q^{o}$ leads to

$$\sum_\upsilon \frac{C_\upsilon{}^2}{(\omega^2-\omega_\upsilon{}^2)} \left[\left[Z_\alpha + \sum_{j,\sigma} \frac{2F_{j\sigma}^2(\vec{Q}_\alpha)\ \epsilon_j}{(\omega^2-\epsilon_j{}^2)} \right] \left[1 - \left[\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q} \right]^2 \right] + \omega^2 \right.$$

$$\left. - \frac{\partial E_{o,HF}(\vec{Q}_\alpha)}{\partial Q}\ \frac{\partial^2\varepsilon_{a\sigma}(Q_\alpha,\ q_\alpha)}{\partial q^2} - \frac{\partial^2 V_o(q_\alpha)}{\partial q^2} \right] = 1 \tag{C.9}$$

For $\alpha = 1$ or 3 all the normal modes of Hamiltonian are stable. For $\alpha = 2$, one mode is unstable. We donote the corresponding frequency by Ω_{na}. Putting $\omega^2 = -\Omega_{na}{}^2$ in the equation (C.9), we obtain the frequency of the unstable mode. By using the definition of $J(\omega)$, solvent spectral function, equation (37) and $D_\alpha(\omega)$, electronic spectral function, defined by

$$D_\alpha(\omega) = \sum_{j,\sigma} \left| F_{j\sigma}(\vec{Q}_\alpha) \right|^2 \delta(\omega - \epsilon_j)$$

$$= 2\int_{\varepsilon_F}^{\varepsilon_F+\omega} d\varepsilon\ \rho_a^\sigma(\varepsilon,\ \vec{Q}_\alpha)\ \rho_a^\sigma(\varepsilon-\omega,\ \vec{Q}_\alpha) \tag{C.10}$$

in the equation (C.9) we can show that Ω_{na} obeys the equation,

$$\left[\left[E''_{o,HF}(\vec{\bar{Q}}_{\alpha}) - 2\Omega_{na}^{2} \int_{0}^{\infty} \frac{d\omega_1 \; D_{\alpha}(\omega_1)}{\omega_1(\omega_1^2 + \Omega_{na}^{2})} \left[1 - \left(\frac{\partial \varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})}{\partial q} \right)^{2} \right] \right] - \Omega_{na}^{2} \right.$$

$$\left. - \frac{\partial E_{o,HF}(\vec{\bar{Q}}_{\alpha})}{\partial Q} \; \frac{\partial^2 \varepsilon_{a\sigma}(Q_{\alpha},\ q_{\alpha})}{\partial q^2} - \frac{\partial^2 V_o(q_{\alpha})}{\partial q^2} \right] \frac{2}{\pi} \int_{0}^{\infty} \frac{d\omega \; \omega \; J(\omega)}{(\omega^2 + \Omega_{na}^{2})} = 1 \ . \tag{C.11}$$

Using the definitions of $J(\omega)$ and $D_{\alpha}(\omega)$, we get the equation (71) in the text.

(2) Evaluation of p_n

Just as in Appendix A,

$G^{(\alpha)} = G_o + G_1^{(\alpha)}$ and defining

$$G_o = \begin{bmatrix} \omega_{\upsilon}^{2}\delta_{\upsilon\upsilon_1} & 0 & 0 \\ 0 & \omega_{\alpha}^{2} & 0 \\ 0 & 0 & \epsilon_j^{2}\delta_{\sigma\sigma_1} \end{bmatrix} \tag{C.12}$$

and

$$G_1^{(\alpha)} = \begin{bmatrix} Z_{\alpha}C_{\upsilon}C_{\upsilon}' & Z_{\alpha}\left(\frac{\partial \varepsilon_{a\sigma}(Q_{\alpha},q_{\alpha})}{\partial q}\right) C_{\upsilon} & F_{j\sigma}(Q_{\alpha},\ q_{\alpha})\sqrt{2\epsilon_j}\ C_{\upsilon} \\ Z_{\alpha}\left(\frac{\partial \varepsilon_{a\sigma}(Q_{\alpha},q_{\alpha})}{\partial q}\right) C_{\upsilon} & 0 & F_{j\sigma}(Q_{\alpha},\ q_{\alpha})\sqrt{2\epsilon_j}\frac{\partial \varepsilon_{a\sigma}(Q_{\alpha},q_{\alpha})}{\partial q} \\ F_{j\sigma}(Q_{\alpha},\ q_{\alpha})\sqrt{2\epsilon_j}\ C_{\upsilon} & F_{j\sigma}(Q_{\alpha},q_{\alpha})\sqrt{2\epsilon_j}\left(\frac{\partial \varepsilon_{a\sigma}(Q_{\alpha},q_{\alpha})}{\partial q}\right) & 0 \end{bmatrix} \tag{C.13}$$

we can write

$$\ln p_n = \mathrm{Tr}\ \ln\left[1+(n^2 I + Z^2 G_o)^{-1} Z^2 G_1^{(2)}\right] - \mathrm{Tr}\ \ln\left[1+(n^2 I+G_o)^{-1} Z^2 G_1^{(1)}\right]. \tag{C.14}$$

To evaluate $\mathrm{Tr}\ \ln\left[1+(n^2 I+Z^2 G\ )^{-1} Z^2 G^{(\alpha)}\right]$ we adopt the following procedure.

We introduce an $(N+2M+1)$ dimensional inner product space $\mathscr{H}$ spanned by orthonormal set of vectors $|h_1\rangle$, $|h_2\rangle$, $\ldots,|h_\upsilon\rangle\ldots.|h_N\rangle$, $|b_{1\sigma}\rangle$, $|b_{2\sigma}\rangle,\ldots\ldots,|b_{\upsilon\sigma}\rangle\ldots.,|b_{M\sigma}\rangle$, and $|h\rangle$ and introduce operators $\hat{G}^{(\alpha)}$, $\hat{G}_o$ and $\hat{G}_1^{(\alpha)}$ such that $G^{(\alpha)}$, G_o and $G_1^{(\alpha)}$ are matrix representation of these operators in the above basis. For example,

$$\langle h_\upsilon|\hat{G}^{(\alpha)}|b_{j\sigma}\rangle = [G^{(\alpha)}]_{\upsilon j\sigma}.$$

Now we define

$$|Q\rangle = \sum_\upsilon C_\upsilon |h_\upsilon\rangle\ ,$$

$$|R\sigma\rangle = \sum_j F_{j\sigma}(Q_\alpha,\ q_\alpha)|b_{j\sigma}\rangle \sqrt{2\epsilon_j} \tag{C.15}$$

and

$$|\bar{Q}\rangle = \langle Q|Q\rangle^{-1/2}|Q\rangle$$

$$|\bar{R}\sigma\rangle = \langle R\sigma|R\sigma\rangle^{-1/2}|R\sigma\rangle\ . \tag{C.16}$$

$|\bar{Q}\rangle$ and $|\bar{R}\sigma\rangle$ span a four-dimensional subspace of $\mathscr{H}$ and the projection operator on to this space is

$$\hat{P} = |\bar{Q}\rangle\langle\bar{Q}| + \sum_\sigma |\bar{R}\sigma\rangle\langle\bar{R}\sigma| + |h\rangle\langle h|. \tag{C.17}$$

It obeys $\hat{P}^2 = \hat{P}$. Inspection shows that the operator $\hat{G}^{(\alpha)}$ can be written as

$$\hat{G}_1^{(\alpha)} = |Q\rangle Z_\alpha \langle Q| + |Q\rangle\langle h| Z_\alpha \left(\frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q}\right) + |h\rangle\langle Q| Z_\alpha \left(\frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q}\right) + \sum_\sigma |Q\rangle\langle R\sigma|$$

$$+ \sum_\sigma |R\sigma\rangle\langle Q| + \sum_\sigma |R\sigma\rangle\langle h| \left(\frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q}\right) + \sum_\sigma |h\rangle\langle R\sigma \left(\frac{\partial \varepsilon_{a\sigma}(Q_\alpha, q_\alpha)}{\partial q}\right) . \qquad (C.18)$$

This operator, obviously has the property that

$$\hat{G}_1^{(\alpha)} = \hat{P}\hat{G}_1{}^{(\alpha)}\hat{P} .$$

Expanding the logarithmic function, we get

$$\mathrm{Tr}\ \ln\left[1+(n^2 I+Z^2 G_0)^{-1}\ Z^2 G_1^{(\alpha)}\right]$$

$$= \mathrm{Tr} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m}\ Z^{2m}\ \left((n^2+Z^2\hat{G}_0)^{-1}\hat{P}\hat{G}_1{}^{(\alpha)}\right)^m . \qquad (C.19)$$

Putting $\hat{G}_1^{(\alpha)} = \hat{P}\hat{G}_1^{(\alpha)}\hat{P}$ and using the cyclic invariance of the trace, we get

$$\mathrm{Tr}\ \ln\left[1+(n^2 I+Z^2 G_0)^{-1} Z^2 G_1{}^{(\alpha)}\right]$$

$$= \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m}\ Z^{2m}\ \mathrm{Tr}\left[\hat{P}(n^2+Z^2\hat{G}_0)^{-1}\hat{P}\hat{G}_1^{(\alpha)}\right]^m$$

$$= \mathrm{Tr}\ \ln\left[1+Z^2\hat{P}(n^2+Z^2\hat{G}_0)^{-1}\hat{P}\ \hat{G}_1^{(\alpha)}\right] . \qquad (C.20)$$

Defining $X_\alpha(n)$ by

$$\ln X_\alpha(n) = \mathrm{Tr}\ \ln\left[1+Z^2\hat{P}(n^2+Z^2\hat{G}_o)^{-1}\hat{P}\hat{G}_1{}^{(\alpha)}\right] , \tag{C.21}$$

we obtain

$$p_n = \frac{X_1(n)}{X_2(n)} ,$$

where

$$X_\alpha(n) = \exp\left[\mathrm{Tr}\ \ln\ (1+\hat{P}(n^2+Z^2\hat{G}_o)^{-1}\hat{P}\hat{G}_1{}^{(\alpha)}\right]$$

$$= \det\left[1+\hat{P}(n^2+Z^2\hat{G}_o)^{-1}\hat{P}\hat{G}_1{}^{(\alpha)}\right] . \tag{C.22}$$

To calculate the determinant, we have to find the matrix of the operator $\left[1+\hat{P}(n^2+Z^2\hat{G}_o)^{-1}\hat{P}\hat{G}_1^{(\alpha)}Z^2\right]$. This is conveniently done in a new orthonormal basis with $|\overline{Q}>$, $|h>$ and $|\overline{R}\sigma>$ as the first four vectors, the remaining being orthogonal to them. Then we get

$X_\alpha(n) =$

$$\begin{vmatrix}
1+Z^2\bar{G}_{oQ}^{-1} Z_\alpha & Z^2\langle Q|Q\rangle^{-1/2}\bar{G}_{oQ}^{-1} \times Z_\alpha\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q}\right) & Z^2\langle Q|Q\rangle^{-1/2}\bar{G}_{oQ}^{-1} \times \langle R\sigma|R\sigma\rangle^{1/2} & Z^2\langle Q|Q\rangle^{-1/2}\bar{G}_{oQ}^{-1} \times \langle R\sigma|R\sigma\rangle^{1/2} \\
Z^2\bar{G}_{oh}^{-1} Z_\alpha \times\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q}\right)\langle Q|Q\rangle^{1/2} & 1 & Z^2\bar{G}_{oh}^{-1}\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q}\right) \times \langle R\sigma|R\sigma\rangle^{1/2} & Z^2\bar{G}_{oh}^{-1}\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q} \times \langle R\sigma|R\sigma\rangle^{1/2} \\
Z^2\langle R\sigma|R\sigma\rangle^{-1/2}\bar{G}_{oR}^{-1} \times \langle Q|Q\rangle^{1/2} & Z^2\langle R\sigma|R\sigma\rangle^{-1/2} \times \bar{G}_{oR}^{-1}\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q}\right) & 1 & 0 \\
Z^2\langle R\sigma|R\sigma\rangle^{-1/2}\bar{G}_{oR}^{-1} \times \langle Q|Q\rangle^{1/2} & Z^2\langle R\sigma|R\sigma\rangle^{-1/2} \times \bar{G}_{oR}^{-1}\left(\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q}\right) & 0 & 1
\end{vmatrix}$$

which is a 4x4 determinant.

(C.23

where

$$\bar{G}_{oQ}^{-1} = \langle Q|(n^2+Z^2G_o)^{-1}|Q\rangle$$

$$\bar{G}_{oh}^{-1} = \langle h|(n^2+Z^2G_o)^{-1}|h\rangle$$

and

$$\bar{G}_{oR}^{-1} = \langle R\sigma|(n^2+Z^2G_o)^{-1}|R\sigma\rangle\ .$$

The matrix elements can be evaluated to obtain

$$X_\alpha(n) = 1 + \sum_\upsilon \frac{C_\upsilon^{\,2}}{(n^2Z^{-2}+\omega_\upsilon^{\,2})} \left[E''_{o,HF}(\vec{\overline{Q}}_\alpha) + 2n^2Z^{-2}\sum_{j,\sigma} \frac{F_{j\sigma}^{\,2}(\vec{\overline{Q}}_\alpha)}{\epsilon_j(n^2Z^{-2}+\epsilon_j^{\,2})}\right]$$

$$+ \frac{1}{(n^2Z^{-2}+W_\alpha^{\,2})} \left[\frac{\partial\varepsilon_{a\sigma}(Q_\alpha,q_\alpha)}{\partial q}\right]^2 \left[E''_{o,HF}(\vec{\overline{Q}}_\alpha) + 2n^2Z^{-2}\sum_{j,\sigma} \frac{F_{j\sigma}^{\,2}(\vec{\overline{Q}}_\alpha)}{\epsilon_j(n^2Z^{-2}+\epsilon_j^{\,2})}\right].$$

(C.24)

This is the equation (77) in the text. Using the definitions of $J(\omega)$ and $D_\alpha(\omega)$ as

$$J(\omega) = \frac{\pi}{2}\sum_\upsilon \frac{C_\upsilon^2}{\omega_\upsilon}\,\delta(\omega-\omega_\upsilon) \quad ; \quad \sum_\upsilon \frac{C_\upsilon^{\,2}}{(n^2Z^{-2}+\omega_\upsilon^{\,2})} = \int_0^\infty \frac{\omega\, J(\omega)\,d\omega}{(n^2Z^{-2}+\omega^2)}$$

and

$$D_\alpha(\omega) = \sum_{j,\sigma} F_{j\sigma}^{\,2}(\vec{\overline{Q}}_\alpha)\,\delta(\omega-\omega_j) \quad ; \quad \sum_{j,\sigma} \frac{F_{j\sigma}^{\,2}(\vec{\overline{Q}}_\alpha)}{\epsilon_j(n^2Z^{-2}+\epsilon_j^{\,2})} = \int_0^\infty \frac{D_\alpha(\omega_1)\,d\omega_1}{\omega_1(n^2Z^{-2}+\omega_1^2)} \quad ,$$

we have arrived at the equation (78) in the text.

(3) Expression for $D_\alpha(\omega)$

Putting the definitions of $F_{j\sigma}(\vec{Q}_\alpha)$ and ϵ_j into the one for $D_\alpha(\omega)$, we get

$$D_\alpha(\omega) = \sum_{\substack{m_> \\ \sigma}} \sum_{m_<} |\langle \psi_{m_> \sigma \vec{Q}_\alpha} | a\sigma \rangle|^2 \; |\langle \psi_{m_< \sigma \vec{Q}_\alpha} | a\sigma \rangle|^2 \delta(\omega - \varepsilon_{m_>} + \varepsilon_{m_<})$$

$$= 2\int_{\varepsilon_F}^{\infty} d\varepsilon_1 \int_{-\infty}^{\varepsilon_F} d\varepsilon_2 \; \rho_a^\sigma(\varepsilon_1, \vec{Q}_\alpha) \; \rho_a^\sigma(\varepsilon_2, \vec{Q}_\alpha) \delta(\omega - \varepsilon_1 + \varepsilon_2)$$

$$= 2\int_{\varepsilon_F}^{\varepsilon_F + \omega} d\varepsilon_1 \; \rho_a^\sigma(\varepsilon_1, \vec{Q}_\alpha) \; \rho_a^\sigma(\varepsilon_1 - \omega, \vec{Q}_\alpha) \; . \qquad \text{(C.25)}$$

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CHAPTER V

CONCLUSION

We have studied the theory of electrochemical charge transfer processes.

The focus of our study of outer sphere electrochemical electron transfer reactions is the shift of the ionic orbital, caused by its interaction with the polarization of the surrounding solvent. In the adiabatic limit, using a path integral approach, we show explicitly that the shift obeys a stochastic integral equation. In certain cases, this may be converted into a stochastic differential equation. This may then be analysed using standard methods to obtain an expression for the rate. The expression so obtained includes correction factors to that obtained by Schmickler. Extension of this work reported here have beeen made[1,2].

We have also analysed electrochemical proton transfer reaction. Here, in addition to the shift Q, q the distance of the proton from the surface, also plays an important role in the dynamics of the process. There is a fairly strong interaction between the nuclear motion and the electronic system and hence the dynamics of the system has to be thought of as taking place on a continuum of potential energy surfaces. A bosonisation technique has been used for this purpose and an expression for the rate has been derived.

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