# QUANTUM MECHANICAL APPROACHES TOWARDS UNDERSTANDING CHARGE TRANSFER IN CHEMICAL SYSTEMS

A Dissertation

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## QUANTUM MECHANICAL APPROACHES TOWARDS UNDERSTANDING CHARGE TRANSFER IN CHEMICAL SYSTEMS

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The transfer of electrons from one entity to another, the former – the electron donor and the latter – the electron acceptor, is one of the most fundamental processes in nature. Important examples being that of electron transfer in photosynthesis, respiration, chemical reactions, photocatalysts, and photovoltaic devices, to name a few. The electron transfer (ET) rate and mechanism is dictated by the strength of the interaction between the donor and acceptor, the temperature, and the external environment.

An exact quantum mechanical description is precluded by the exponential scaling of the computation with the number of particles in the system. The path integral formulation to solve the time-dependent Schrödinger equation ails from the same problem; however, it is has been used to derive approximate, but rigorous semiclassical theories in real and imaginary time which can incorporate dynamical and statistical quantum mechanical effects such as zero point energy, tunneling, and interference into classical molecular dynamics simulations.

For ET occurring at low temperatures, the dominant mechanism is quantum tunneling. The determination of the optimal tunneling pathway – the instanton – and its use in the computation of the ET rate for systems where the electron donor and acceptor are strongly coupled has been extensively studied. Recently, a ring polymer instanton (RPI) – a discrete approximation to the continuous instanton path – was proposed; the difficult trajectory search encountered in semiclassical instanton theory was reformulated as a multidimensional optimization problem.

The work presented in this dissertation is geared towards understanding ET at low temperatures, but for systems where the coupling between the electron donor and acceptor is weak, i.e., in the nonadiabatic limit. It elaborates on extending the RPI formulation to multi-state systems, and demonstrates the utility of the multistate ring polymer instanton (MS-RPI) in the computation of nonadiabatic ET rates. Furthermore, the effects of an external bath on the RPI is investigated and its use in the determination of a reaction rate in model systems is demonstrated via both system-bath and reduced dimensional formulations. It is shown that the optimal tunneling path for molecular systems containing conical intersections (accidental degeneracies of the adiabatic eigenstates) can be obtained using the MS-RPI formulation. The discussion of the experimentally observed conductivity of two-dimensional Fe and Cr metal-organic frameworks, and the efforts to explain the them is presented next. This is followed by preliminary results obtained for the extension of the RPI method to multi-dimensional systems, and the use of path sampling methods for RPMD. The thesis concludes with a summary and notes on future directions.

### **BIOGRAPHICAL SKETCH**

Srinath was born in Bangalore, India. He moved to Mumbai to pursue undergraduate studies at the Indian Institute of Technology - Bombay, graduating in 2014. Followed by a year long stint with Prof. Ravindra Venkatramani, at the Tata Institute of Fundamental Research – Mumbai, he moved to Ithaca to pursue graduate studies at Cornell University under the guidance of Prof. Nandini Ananth. To Amma, Appa, and Srikanth

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The constant encouragement and indelible support of my parents and brother is central to both the work that I have been able to do, and to who I am. Their constant reminder:

## कर्मण्येवाधिकारस्ते मा फलेषु कदाचन । मा कर्मफलहेत्र्भूमां ते संगोऽस्त्वकर्मणि ॥

as held me in good stead during graduate school. It is to them that I dedicate the work done in this thesis.

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## CHAPTER 1 INTRODUCTION

#### 1.1 Charge transfer phenomena

Charge transfer (CT) lies at the heart of some of the most important chemical and biological processes: respiration [1], photosynthesis [2]; molecular catalysis [3]. The technological advances towards making efficient batteries [4], solar energy conversion [5], depend on a sound understanding of these processes. Refs. [6–10] provide an overview of the theoretical approaches developed towards the study of charge transfer processes.

One of the most common approaches to the modeling of CT processes is to construct system-bath models. A key reason for the development of these systembath models is that only a few modes, of the many present in chemical systems, typically contribute directly to CT. The reduction in dimensionality allows for a more convenient and accurate theoretical analysis. The CT system is divided into two sub-parts: the 'system' and 'bath', followed by the identification of the units that donate and accept the charge – called the donor and acceptor, hereon. The description of the 'system' is complete once the modes coupled to CT from donor to acceptor occurs, are identified; the identification of the modes is a hard problem, in and of itself, for large chemical systems. The modes excluded from the 'system' description are classified as the external bath that interacts with the CT 'system' modes.

Considering the specific case of bimolecular ET in solution, the 'system' comprises of two molecules, one of which is the donor and the other, the acceptor. The ET reaction is described using a solvent coordinate and the system potentials are defined along it; the other solvent modes constitute the bath.

The rate and mechanism of electron transfer (ET) is dependent on: (1) the strength of coupling between the electron donor and the electron acceptor – whether ET is adiabatic or nonadiabatic; (2) the temperature of the system – whether it is a thermally activated process or does ET occur via tunneling; (3) the strength of the coupling of the ET coordinate to the bath degrees of freedom (dofs). A rich variety of behaviors arise due to the interplay of these parameters. Some parameter regimes are easier to study theoretically than experimentally; especially, systems where ET occurs via quantum mechanical tunneling, which occurs at low temperatures. The development of theoretical methods to accurately describe tunneling in ET systems is, thus, of interest to the theoretical chemistry community.

#### **1.2** Real and imaginary time path integrals

Feynman's path integral (PI) approach to QM provides an alternate approach to the computation of the wavefunction [11]. The final wavefunction  $\psi_t(x_N)$  can be obtained by the propagation of the initial wavefunction  $\psi_0(x_0)$  as:

$$\psi_t(x_N) = \langle x_N | \psi_t \rangle = \langle x_N | e^{-\hat{H}t/\hbar} | \psi_0 \rangle = \int \mathrm{d}x_0 \langle x_N | e^{-i\hat{H}t/\hbar} | x_0 \rangle \langle x_0 | \psi_0 \rangle.$$
(1.1)

The matrix element  $\langle x_N | e^{-i\hat{H}t/\hbar} | x_0 \rangle$  is called the 'kernel' and is the probability amplitude associated with a particle starting at  $x_0$  at time 0, reaching  $x_N$  at time t. The kernel can be computed by writing the propagator as a product of N short-time propagators – each propagating the wavefunction for  $\Delta t = t/N$ , and evaluating them in the position basis, effectively integrating over all possible positions of the particle at intermediate times:

$$\langle x_N | e^{-i\hat{H}t/\hbar} | x_0 \rangle = \int d\{x_i\} \prod_{i=0}^{N-1} \langle x_{i+1} | e^{-i\hat{H}\Delta t/\hbar} | x_i \rangle, \qquad (1.2)$$

where  $\int d\{x_i\} \equiv \int dx_1 \int dx_2 \dots \int dx_N$  Consider a one-dimensional Hamiltonian,

$$\hat{H} = \frac{\hat{p}^2}{2M} + V(\hat{x}).$$
(1.3)

Upon evaluating the short-time propagators using Trotter splitting, the matrix element can be rewritten as an integral over all the possible paths, x(t), connecting  $x_N$  and  $x_0$ :

$$\langle x_N | e^{-i\hat{H}t/\hbar} | x_0 \rangle = \int \{ \mathrm{d}x_i \} e^{iS(\{x_i\})/\hbar} \quad \text{where,}$$
 (1.4)

$$S(\{x_i\}) = \sum_{i=0}^{N-1} \left[ \frac{M}{2\Delta t^2} (x_{i+1} - x_i)^2 - V(x_i) \right]$$
(1.5)

In the limit  $N \to \infty$ , this can be written as a path integral:

$$\langle x_N | e^{-i\hat{H}t/\hbar} | x_0 \rangle = \int \mathcal{D}[x(t)] e^{iS[x(t)]/\hbar}$$
 where, (1.6)

$$\mathcal{S}[x(t)] = \int_0^t dt' \left[ \frac{M}{2} \left( \frac{dx(t')}{dt'} \right)^2 - V(x(t')) \right]$$
(1.7)

The weight associated with each path is  $e^{iS[x(t)]/\hbar}$ , where S[x(t)] is the classical action of the path – the time integral of the Lagrangian. Exact quantum [12] and semiclassical methods [13] based on real-time PIs, have been proposed. Semiclassical methods rely on the fact that for large systems the action associated with a path, in systems of chemical interest, is large compared to  $\hbar$ , making  $e^{iS[x(t)]/\hbar}$  high oscillatory. The destructive interference due to the phase cancels out the contributions from most paths and the major contributors to the integral are classical paths that extremize the action  $\delta S[x_{cl}(t)] = 0$ , and that are governed by the familiar Euler-Lagrange equation:

$$M\left(\frac{d^2x(t)}{dt^2}\right) = -\frac{dV}{dx}.$$
 (1.8)

The quantum fluctuations about this classical path can be included using a Taylor expansion of the action S[x(t)], upto second order, about this extremum, followed by integration of the resulting gaussian terms, effectively 'sewing quantum flesh on classical bones' [14]. This is one way to approximately include QM effects such as zero point energy, tunneling, and interference effects in classical molecular dynamics (MD) simulations.

The study of real time dynamics of a molecular systems using exact quantum methods is made difficult by the exponential scaling of the quantum mechanical wavefunction. Thus, the systems studied are, typically, low dimensional or model systems; however, extensions to realistic systems have been attempted recently [15]; semiclassical methods based on the initial value representation (IVR) show promise towards the study of large-scale molecular systems [16]. The IVR trick converts a boundary value problem – the search for trajectories starting at  $x_0$ and ending at  $x_N$  – into a more convenient initial value problem, where one propagates classical trajectories given initial phase space points. Unfortunately, these tricks do not alleviate the problems posed by the dynamical sign. The computation of correlation functions instead of propagators themselves along with the use of the Filinov filtration technique, makes this slightly more manageable. The Filinov filter excludes paths with highly oscillatory phase which contribute, in effect, negligibly to the computation of the correlation function. Recent advances provide hope for the accurate long time simulation of realistic molecular systems [17].

When only the equilibrium statistical properties of a quantum system, described by Eq. 1.3, are of interest, the imaginary time PI formalism proves more useful. This is obtained by performing a Wick rotation; equivalently, setting  $\beta \equiv -it/\hbar$  in the propagator in Eq. 1.1 to get the quantum Boltzmann operator. The canonical partition function  $\mathcal{Z}$  can be obtained as its trace, evaluated it in the position basis:

$$\mathcal{Z} = \operatorname{Tr}[e^{-\beta \hat{H}}] = \int_{N/2} \mathrm{d}x \langle x| \left(e^{-\beta \hat{H}/N}\right)^N |x\rangle$$
(1.9)

$$\mathcal{Z} = \lim_{N \to \infty} \mathcal{Z}_{\text{RP}} = \lim_{N \to \infty} \left( \frac{MN}{2\pi\beta} \right)^{N/2} \int \{ dx_{\alpha} \} e^{-\beta_N V_{\text{RP}}(\{x_{\alpha}\})} \quad \text{where,} \qquad (1.10)$$

$$V_{\rm RP}(\{x_{\alpha}\}) = \sum_{\alpha=1}^{N} \left[ \frac{MN^2}{2\beta^2} (x_{\alpha+1} - x_{\alpha})^2 + V(x_{\alpha}) \right], \tag{1.11}$$

and  $\beta_N \equiv \beta/N$ . The equilibrium statistics of a quantum particle is equivalent to that of a classical ring polymer (RP) governed by the potential  $V_{\text{RP}}(\{x_{\alpha}\})$ . In the limit of an infinite number of beads (imaginary time slices), this reduces to a PI expression for  $\mathcal{Z}$ :

$$\mathcal{Z} = \int \mathcal{D}[x(\tau)] e^{-\mathcal{S}[x(\tau)]}, \qquad (1.12)$$

$$S[x(\tau)] = \int_0^\beta d\tau \left[ \frac{M}{2} \left( \frac{dx(\tau)}{d\tau} \right)^2 + V[x(\tau)] \right]$$
(1.13)

Here, the integral is over circular paths (periodic orbits) that begin at x at  $\tau = 0$ and end at x at  $\tau = \beta$ , and whose contribution to the integral is determined by an exponentially decaying function of the Euclidean action. The Euler-Lagrange equations take the form:

$$M\left(\frac{d^2x(\tau)}{d\tau^2}\right) = \frac{dV}{dx}.$$
 (1.14)

In Eq. 1.14, we see that the particle moves on the inverted potential. To illustrate its utility, consider the harmonic potential defined by:

$$V_{\text{QHO}} = \frac{1}{2}m\omega^2 x^2, \qquad (1.15)$$

which in the imaginary time formalism becomes a harmonic barrier. The classical path is just the particle at the top of the barrier  $x_{cl}(\tau) = 0$ . Expanding the euclidean

action about this stationary path up to second order and integrating, the canonical partition function for the quantum harmonic oscillator is obtained:

$$\mathcal{Z}_{\text{QHO}} = \frac{1}{2\sinh(\beta\omega/2)} \tag{1.16}$$

The canonical partition in Eq. 1.10 can be written as a phase space integral by the introduction of momentum integrals:

$$\mathcal{Z}_{\text{RP}} = \lim_{N \to \infty} \int d\{p_{\alpha}\} d\{x_{\alpha}\} e^{-\beta_N H_{\text{RP}}(\{x_{\alpha}, p_{\alpha}\})} \quad \text{where,} \qquad (1.17)$$

$$H_{\rm RP}(\{x_{\alpha}, p_{\alpha}\}) = \sum_{\alpha=1}^{N} \left[ \frac{p_{\alpha}^2}{2M} + \frac{MN^2}{2\beta^2} (x_{\alpha+1} - x_{\alpha})^2 + V(x_{\alpha}) \right].$$
(1.18)

The positions and momenta of the RP can be propagated in time using Hamilton's equations:

$$\frac{dx_{\alpha}}{dt} = \frac{\partial H_{\rm RP}}{\partial p_{\alpha}} = \frac{p_{\alpha}}{M},\tag{1.19}$$

$$\frac{dp_{\alpha}}{dt} = -\frac{\partial H_{\rm RP}}{\partial x_{\alpha}} = -\frac{M}{\beta_N^2} (2x_{\alpha} - x_{\alpha+1} - x_{\alpha-1}).$$
(1.20)

Path integral molecular dynamics (PIMD) uses the fictitious dynamics generated by this RP hamiltonian,  $H_{\rm RP}$  to sample the phase space of the ring polymer. Kubotransformed quantum correlation functions (QCF),

$$\tilde{C}_{AB}(t) = \frac{1}{\beta \mathcal{Z}} \int_0^\beta \operatorname{Tr} \left[ e^{-(\beta - \lambda)\hat{H}} \hat{A}(0) e^{-\lambda \hat{H}} \hat{B}(t) \right] \mathrm{d}\lambda, \qquad (1.21)$$

can be computed using the RPMD approximation:

$$\tilde{C}_{AB}(t) \approx \frac{1}{(2\pi)^N} \int d\{p_{\alpha,0}\} d\{x_{\alpha,0}\} e^{-\beta_N H_{RP}(\{x_{\alpha,0}, p_{\alpha,0}\})} A_N(\{x_{\alpha,0}\}) B_N(\{x_{\alpha,t}\}) \quad (1.22)$$

where

$$A_N(\{x_{\alpha,0}\}) = \frac{1}{N} \sum_{\alpha=1}^N A(x_{\alpha,0})$$
(1.23)

$$B_N(\{x_{\alpha,t}\}) = \frac{1}{N} \sum_{\alpha=1}^N B(x_{\alpha,t})$$
 (1.24)

and it is assumed that operators  $\hat{A}$  and  $\hat{B}$  depend only on position [18]. Here, the time-evolved positions are obtained from the trajectories generated by  $H_{\rm RP}$ . The method neglects real-time quantum coherence, yet can compute QCFs for short times, accurately. RPMD is, thus, most useful in the study of condensed phase systems, where quantum decoherence occurs rapidly.

Nuclear quantum effects are accurately captured by RPMD [19]. The non-zero spread of the RP incorporates zero point energy (ZPE) and delocalization effects of quantum particles; it has been shown that it accurately predicts the rate constant in the shallow and deep tunneling limits. It can also reproduce exact QM results in the high temperature, short time, and harmonic oscillator limits, making it an attractive and easy option towards the inclusion of quantum effects in classical MD simulations of molecular systems. This has led to a surge in the development of RPMD methods for the study of both adiabatic and nonadiabatic systems [18,20].

#### **1.3** Quantum mechanical tunneling and instantons

The radioactive decay of heavy nuclei into lighter nuclei by the emission of alpha particles was explained using the concept of quantum mechanical (QM) tunneling by Gamow [21]. This phenomenon is quite common in nature and not restricted to radioactivity. Recently, the 'quantum tunneling state' of the water molecule was discovered [22]. Experimentally, chemical reaction rates had been observed to reach a constant value as the temperature of the reactive system was lowered, deviating from Arrhenius behavior; it was posited that at these low temperatures, the reaction proceeds via QM tunneling. Thus, the study of tunneling effects in chemical systems at low temperatures has been of interest [23]. As an aside, it is noted that technological advances based on QM tunneling have been made: tunnel diode and scanning tunneling microscope, for example; and, that the accurate reproduction of this thesis and the work described in it, relies on the absence of quantum tunneling in transistors.

Wigner suggested that quantum effects need to be included in classical transition state theory (TST) to get better estimates for the rate constants [24]. A SC theory for the computation of reaction rates was proposed by Miller, using the flux-side correlation function. In the SC limit, the approximation of matrix elements of the Boltzmann operator gives rise to the idea of 'instantons' – classical periodic orbits that exist in the barrier, which are solutions of Eq. 1.14. The simplest approach to understand instantons is by considering a harmonic barrier; in the imaginary time formalism, the dynamics of the particle would then be governed by a harmonic well (c.f. the discussion on imaginary time PI in Sec. 1.2). Thus, at low temperatures, there exists a stationary periodic orbit of period  $\beta$ , in the well; it represents the optimal tunneling pathway for the quantum particle traversing through the classically forbidden barrier. In the high temperature limit,  $\beta \rightarrow 0$ , the instanton shrinks and collapses to the top of the barrier becoming the classical transition state. The temperature at which the dominant reaction mechanism changes from classical thermal activation regime to QM tunneling (the deep-tunneling regime), i.e., the first temperature at which the instanton has a finite spread, is the crossover temperature  $T_c$ .

The semiclassical instanton (SCI) rate constant,  $k_{SCI}$ , obtained from the exact QM flux-side correlation function is:

$$k_{\rm SCI} = \sqrt{\frac{1}{2\pi} \left| \frac{\partial^2 \mathcal{S}[x_{\rm SCI}(\tau)]}{\partial \beta^2} \right|} \frac{e^{-\mathcal{S}[x_{\rm SCI}(\tau)]}}{\mathcal{Z}_r}.$$
 (1.25)

Here,  $x_{SCI}(\tau)$  is the SCI and  $S[x_{SCI}(\tau)]$  is its action; the prefactor is obtained by

performing a steepest descent approximation in the energy space; more details can be found in Ref. [25]. SCIs had been used previously in the computation of the rate of escape from metastable wells, in conjunction with the "Im F" approach by Coleman [26], Affleck [27] and others [28, 29].

The "Im F" premise relates the tunneling rate to the quantum Boltzmann operator computed in the vicinity of the barrier. Consider the analytical continuation of the Hamiltonian of the system to the complex plane, its eigenvalues are necessarily complex  $E_j - i\Gamma_j/2$ , where  $E_j$  is the energy of the  $j^{\text{th}}$  bound state and  $\Gamma_j$ , its lifetime. The canonical partition function  $\mathcal{Z}_{AC}$ , for the analytically continued Hamiltonian, in the energy basis [30]:

$$\mathcal{Z}_{AC} = \sum_{j} e^{-\beta(E_k - i\Gamma_j/2)} \approx \sum_{j} e^{-\beta E_j} \left( 1 + i \frac{\beta \Gamma_j}{2} \right), \qquad (1.26)$$

$$\mathcal{Z}_{AC} = \mathcal{Z}_r \left( 1 + i \frac{\beta}{2\mathcal{Z}_r} \sum_j \Gamma_j e^{-\beta E_j} \right)$$
(1.27)

This can be rewritten as:

$$\frac{\operatorname{Im} \mathcal{Z}_{AC}}{\mathcal{Z}_r} = \frac{\beta}{2} \times \frac{\sum_j \Gamma_j e^{-\beta E_j}}{\mathcal{Z}_r}.$$
(1.28)

The last term on the right hand side of Eq. 1.28 is just the tunneling rate written as a sum of thermally weighted decay rates of each bound state j of the reactant, through the barrier; this yields:

$$k(\beta) = \frac{2}{\beta Z_r} \operatorname{Im} Z_{AC} \approx \frac{2}{\beta} \frac{Z_b}{Z_r}, \qquad (1.29)$$

which is the "Im F" approximation [31]. Here,  $\mathcal{Z}_b$  and  $\mathcal{Z}_r$  are the barrier and reactant partition functions, respectively. Discrete approximations to the SCI have been proposed [32–39] to study both adiabatic and nonadiabatic model and realistic systems; the ring polymer instanton (RPI) is more amenable to numerical computation [40], and its determination and utility in the computation of the rate is described in the next section.

#### **1.4** Ring polymer instanton and reaction rates

The canonical rate constant  $k_{\text{RPI}}$  can be obtained using the 'Im F' model as described in Eq. 1.29. Considering the system described by a 1D Hamiltonian, the canonical partition function and the ring polymer potential are given by Eqs. 1.10 and 1.11, respectively. The barrier partition function  $\mathcal{Z}_b$  in Eq. 1.29, is computed using the RPI – a first order saddle point on the RP potential. The N beads of the RP must satisfy the stationarity condition:

$$\frac{M}{\beta_N^2}(2x_\alpha - x_{\alpha-1} - x_{\alpha+1}) + V'_{\rm RP}(x_\alpha) = 0, \quad \alpha = 1, 2, \dots, N \quad , \tag{1.30}$$

and the diagonalization of the hessian of the RP potential,

$$\frac{\partial^2 V_{\text{RP}}}{\partial x_{\mu} \partial x_{\nu}} = \frac{M}{\beta_N^2} (2\delta_{\mu,\nu} - \delta_{\mu,\nu-1} - \delta_{\mu,\nu+1}) + V_{\text{RP}}'' \delta_{\mu,\nu} \qquad \mu, \nu = 1, \dots, N,$$
(1.31)

evaluated at the RPI configuration ( $\bar{\mathbf{x}} \equiv \{\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N\}$ ) must yield one negative eigenvalue. The invariance of the RP potential to the permutation of the RPI beads, indicates that one of the eigenvalues must be zero. The barrier partition can be evaluated via a steepest descent approximation by expanding the RP potential about the RPI configuration:

$$\mathcal{Z}_{b} = \lim_{N \to \infty} \left( \frac{MN}{2\pi\beta} \right)^{N/2} e^{-\beta_{N} V_{\text{RP}}(\bar{\mathbf{x}})} \int \{ dx_{\alpha} \} \exp\left[ -\beta_{N} (\mathbf{x} - \bar{\mathbf{x}})^{T} \frac{V_{\text{RP}}''(\bar{\mathbf{x}})}{2} (\mathbf{x} - \bar{\mathbf{x}}) \right], (1.32)$$
$$\mathcal{Z}_{b} = \lim_{N \to \infty} \left( \frac{MN}{2\pi\beta} \right)^{N/2} e^{-\beta_{N} V_{\text{RP}}(\bar{\mathbf{x}})} \int \{ dy_{\alpha} \} \exp\left[ -\frac{M\beta_{N}}{2} \sum_{\alpha=1}^{N} \lambda_{\alpha}^{2} y_{\alpha}^{2} \right].$$
(1.33)

where Eq. 1.33 is obtained from Eq. 1.32 upon diagonalization;  $\lambda_{\alpha}$  is the eigenvalue, and  $y_{\alpha}$  the corresponding eigenvector. The integration of  $y_1$  – the unstable mode corresponding to the negative eigenvalue  $\lambda_1$ , is carried out along the positive half of the imaginary axis;  $y_2$  – the zero eigenvalue mode is integrated out analytically; the rest are standard gaussian integrals. The rate constant is determined

by substituting this approximation to  $\mathcal{Z}_b$ :

$$k_{\rm RPI}(\beta) \approx \frac{2}{\beta} \frac{Z_b}{Z_r} = \frac{1}{\beta_N} \sqrt{\frac{M_{Z_N}}{2\pi\beta_N}} \frac{e^{-\beta_N V_{\rm RP}(\bar{\mathbf{x}})}}{Z_r} \prod_{\alpha=1}^N \frac{1}{\beta_N |\lambda_\alpha|}.$$
 (1.34)

Here, the ' indicates that  $\lambda_2$  is excluded from the product, and  $z_N = \sum_{\alpha} (\bar{x}_{\alpha} - \bar{x}_{\alpha+1})^2$ is obtained by the integration of the zero mode. It is noted that in the limit of infinite beads,  $\beta_N \rightarrow d\tau$ ; therefore, the ring polymer potential at the instanton configuration is the same as the classical action associated with the SCI:

$$\lim_{N \to \infty} \beta_N V_{\text{RP}} = \sum_{\alpha=1}^N \beta_N \left[ \frac{M}{2} \frac{(x_{\alpha+1} - x_\alpha)^2}{\beta_N^2} + V(x_\alpha) \right]$$
(1.35)

$$= \int_0^\beta d\tau \left[ \frac{M}{2} \left( \frac{dx[\tau]}{d\tau} \right)^2 + V[x(\tau)] \right]$$
(1.36)

$$\Rightarrow \lim_{N \to \infty} \beta_N V_{\text{RP}}(\bar{\mathbf{x}}) = S_{\text{SCI}}[x(\tau)]$$
(1.37)

#### **1.5** Outline for the thesis

This dissertation primarily deals with the study of charge transfer in model, and molecular systems. In Chapter 2, an extension of the ring polymer instanton to systems with multiple electronic states and its utility in the computation of nonadiabatic reaction rates is presented; Chapter 3 discusses its extension to condensed phase systems via full dimensional system-bath, and reduced system ring polymer representations. In Chapter 4, preliminary results geared towards the study of multi-dimensional systems are presented: multi-state ring polymer instantons for multi-state systems near a conical intersection, and the combination of transition path sampling with ring polymer molecular dynamics to determine ring polymer transition states. Finally, transitioning to the study of molecular systems, preliminary results from a collaborative work characterizing conductivities of 2D metal-organic frameworks are outlined in Chapter 5. The thesis concludes with a summary of key results and discussion of future directions.

#### CHAPTER 2

## MULTI-STATE SYSTEMS AND NONADIABATIC REACTION RATES

The semiclassical instanton approach has been extended to the multi-state case and the rates determined in both the adiabatic and nonadiabatic coupling limits [36, 41, 42]. Others have developed rate theories specifically geared towards the computation of rates in the nonadiabatic limit [35, 36, 42–44]. Two multi-state ring polymer instanton methods are presented in this chapter: the mean-field, and mapping variable flavors. The latter reports on the electronic populations of each bead and both the methods can be used to accurately determine the nuclear RPI; the MF-RPI is used determine the rates [45].

## 2.1 Classically isomorphic multi-state ring polymers

The potential for a multi-state system with  $\mathcal{K}$  electronic states and f nuclear dofs in the diabatic representation is,

$$\mathbf{V}(\hat{\mathbf{R}}) = \sum_{n,m=1}^{\mathcal{K}} |\psi_n\rangle V_{nm}(\hat{\mathbf{R}}) \langle \psi_m |, \qquad (2.1)$$

where  $\{|\psi_n\rangle\}$  are the diabatic electronic states, the diagonal matrix elements  $V_{nn}(\hat{\mathbf{R}})$ are the potentials corresponding to the  $n^{\text{th}}$  state, and the off-diagonal matrix elements  $V_{nm}(\hat{\mathbf{R}})$  describe the electronic couplings between states n and m. The canonical partition function is expressed as a trace over the Boltzmann operator,

$$\mathcal{Z} = \operatorname{Tr}_{ne}[e^{-\beta\hat{H}}] \propto \lim_{N \to \infty} \int d\{\mathbf{R}_{\alpha}\} e^{-\beta U(\{\mathbf{R}_{\alpha}\})} \operatorname{Tr}_{e}\left[\prod_{\alpha=1}^{N} e^{-\beta_{N} \mathbf{V}(\mathbf{R}_{\alpha})}\right] \quad \text{and}, \quad (2.2)$$

$$U(\{\mathbf{R}_{\alpha}\}) = \frac{1}{N} \sum_{\alpha=1}^{N} \frac{M}{2\beta_{N}^{2}} (\mathbf{R}_{\alpha} - \mathbf{R}_{\alpha+1})^{T} (\mathbf{R}_{\alpha} - \mathbf{R}_{\alpha+1}), \qquad (2.3)$$

where the subscripts n and e indicate that the trace is evaluated over the nuclear and electronic dofs respectively, and  $U(\{\mathbf{R}_{\alpha}\})$  is the inter-bead potential. Eq. 2.2 is obtained by evaluating the trace over the nuclear dofs in the position basis. The trace over electronic dofs can be evaluated in a number of ways [46–50]; here, the MF and one MV formulation with explicit electronic state variables, are explored.

### 2.1.1 Mean field representation

The MF representation of the canonical partition function [35, 41, 47, 49, 51, 52] is obtained by introducing N copies of the identity,

$$\mathbb{1} = \sum_{n} |\psi_n\rangle \langle \psi_n|, \qquad (2.4)$$

in Eq. 2.2 and evaluating the trace to obtain [53]

$$\operatorname{Tr}_{e}\left[\prod_{\alpha=1}^{N} e^{-\beta_{N} \mathbf{V}(\mathbf{R}_{\alpha})}\right] = \operatorname{Tr}\left[\prod_{\alpha=1}^{N} \mathcal{M}(\mathbf{R}_{\alpha}, \mathbf{R}_{\alpha+1})\right] \equiv \Gamma_{\mathrm{MF}},$$
(2.5)

where the matrix elements  $\mathcal{M}(\mathbf{R}_{\alpha}, \mathbf{R}_{\alpha+1})$  are

$$\mathcal{M}_{nn} = e^{-\beta_N/2[V_{nn}(\mathbf{R}_{\alpha})+V_{nn}(\mathbf{R}_{\alpha})]},$$
  
$$\mathcal{M}_{nm} = -\beta_N/4\left[V_{nm}(\mathbf{R}_{\alpha})+V_{nm}(\mathbf{R}_{\alpha+1})\right] \begin{bmatrix} e^{-\beta_N/2[V_{nn}(\mathbf{R}_{\alpha})+V_{nn}(\mathbf{R}_{\alpha+1})]} \\ +e^{-\beta_N/2[V_{mm}(\mathbf{R}_{\alpha})+V_{mm}(\mathbf{R}_{\alpha+1})]} \end{bmatrix}.$$
 (2.6)

The quantum canonical partition function in the MF representation is then

$$\mathcal{Z}_{\mathrm{MF}} \propto \lim_{N \to \infty} \int d\{\mathbf{R}_{\alpha}\} e^{-\beta V_{\mathrm{MF}}(\{\mathbf{R}_{\alpha}\})} \mathrm{sgn}(\Gamma_{\mathrm{MF}})$$
 (2.7)

where  $sgn(\Gamma_{MF})$  ensures that the partition function is positive definite, and the pre-multiplicative constants have been omitted. The effective MF ring polymer potential is

$$V_{\rm MF}(\{\mathbf{R}_{\alpha}\}) = U(\{\mathbf{R}_{\alpha}\}) - \frac{1}{\beta} \ln |(\Gamma_{\rm MF})|, \qquad (2.8)$$

where  $\Gamma_{MF}$ , given in Eq. 2.5, averages over the electronic state configurations of the ring polymer making this a 'mean-field' formulation.

### 2.1.2 Mapping variable representation

Continuous Cartesian variables for the electronic states are introduced using the MMST mapping protocol [54–56]. Specifically, the  $\mathcal{K}$  diabatic electronic states are mapped to a singly excited oscillator (SEO) basis where  $\mathcal{K}-1$  harmonic oscillators are in the ground state and one oscillator (the  $n^{\text{th}}$ ) is in the first excited state,

$$\begin{aligned} |\psi_n\rangle\langle\psi_m| &\to \hat{a}_n^{\dagger}\hat{a}_m \\ |\psi_n\rangle &\to |0_1,\dots,1_n,\dots,0_{\mathcal{K}}\rangle \equiv |n\rangle \end{aligned} \tag{2.9}$$

The resolution of identity in the electronic variables  $(\mathbf{x})$  is [46]

$$\mathbb{1} = \int d\mathbf{x} \, |\mathbf{x}\rangle \langle \mathbf{x}|\mathcal{P},\tag{2.10}$$

where the projection operator  $\mathcal{P} = \sum_n |n\rangle \langle n|$  constrains the electronic coordinates to the SEO subspace.

Introducing multiple copies of this identity and evaluating the electronic trace in Eq. 2.2, an expression for the partition function is obtained [46]:

$$\mathcal{Z}_{\rm MV} \propto \lim_{N \to \infty} \int d\{\mathbf{R}_{\alpha}\} \int d\{\mathbf{x}_{\alpha}\} e^{-\beta V_{\rm MV}} \operatorname{sgn}(\Gamma_{\rm MV}), \qquad (2.11)$$

where

$$\Gamma_{\rm MV} = \operatorname{Tr}\left[\prod_{\alpha=1}^{N} \mathcal{X}_{\alpha} \mathcal{M}(\mathbf{R}_{\alpha}, \mathbf{R}_{\alpha+1})\right], \qquad (2.12)$$

the matrix  $\mathcal{X}_{\alpha} = \mathbf{x}_{\alpha} \otimes \mathbf{x}_{\alpha}^{T}$ , and the MV ring polymer potential is,

$$V_{\rm MV}(\{\mathbf{R}_{\alpha}\}) = U(\{\mathbf{R}_{\alpha}\}) + \frac{1}{\beta} \sum_{\alpha} \mathbf{x}_{\alpha}^T \mathbf{x}_{\alpha} - \frac{1}{\beta} \ln |(\Gamma_{\rm MV})|.$$
(2.13)

#### 2.2 Two-state model systems

The MS-RPI is determined for model systems with two electronic states ( $\mathcal{K} = 2$ ) coupled to one nuclear dof (f = 1), and with three different driving forces; all model systems are in the normal regime of Marcus theory. All parameters are in atomic units, unless specified otherwise. The diagonal elements of the diabatic potential energy matrix,  $\mathbf{V}(\mathbf{R})$ , are

$$V_{ii}(R) = \frac{1}{2}M\omega^2(R-R_i)^2 + \epsilon\delta_{1i},$$
 (2.14)

where  $i = \{1, 2\}$ , the nuclear mass M = 2 a.u., and the oscillator frequency  $\omega = 1$ a.u. In Eq. 2.14, the Kronecker delta,  $(\delta_{1i})$ , indicates that a driving-force  $\epsilon = 0.0, 10.0, 20.0$  a.u. is added to the donor state (left curve), as shown in Fig. 2.1.  $\beta$  is chosen such that it is greater than  $\beta_c$ , such that an instanton solution exists in the adiabatic limit; there is no clear analytical expression for the nonadiabatic crossover temperature [42]. For the systems considered here, in the adiabatic limit  $(\Delta = 5 \text{ a.u.})$ , the barrier frequency  $\omega_b \approx 3$  a.u. is obtained by fitting to an inverted parabola, and this yields  $\beta_c = 2\pi/\omega_b \approx 2$  a.u. for all models [23]. The electronic coupling and inverse temperature ( $\beta$ ) values used here are reported in Table. 2.1.



Figure 2.1: Red (dashed) and grey (continuous) lines show the donor and acceptor states in model I (symmetric system); the green (dotted) and black (dot-dashed) lines represent the donor state in models II and III which are asymmetric systems with  $\epsilon = 10.0$  and 20.0 a.u., respectively.  $R_1$  and  $R_2$  indicate the minima of the donor and acceptor states. Figure has been reproduced from Ref. [45] with permission from the authors.

β	Adiabatic $\Delta$	Nonadiabatic $\Delta$
4.0	5.0	6.25E-3
3.75	5.33	6.67 E-3
3.5	5.71	7.14E-3
3.25	6.15	7.70E-3

Table 2.1: Coupling parameters for models I, II, and III, chosen such that  $\beta\Delta$  remains constant. All values are in atomic units. Table has been reproduced from Ref. [45] with permission from the authors.

#### 2.3 The multi-state ring polymer instanton

#### 2.3.1 The numerical determination of the MS-RPI

The multi-state (MS) RPI (both the MF and MV) is a first order saddle point on the corresponding potential energy surface. In the MF-RP formulation, it is obtained by the simultaneous solution of the fN equations:

$$\frac{\partial V_{\rm MF}}{\partial [\mathbf{R}_{\alpha}]_i} = 0 \tag{2.15}$$

where  $\alpha$  is the bead number index and index *i* runs over the nuclear dofs. Similarly, the MV-RPI is obtained by solving  $(f + \mathcal{K})N$  equations:

$$\frac{\partial V_{\rm MV}}{\partial [\mathbf{R}_{\alpha}]_i} = 0 \text{ and}$$
(2.16)

$$\frac{\partial V_{\rm MV}}{\partial [\mathbf{x}_{\alpha}]_j} = 0, \qquad (2.17)$$

where the index j runs over the electronic states.

The L-BFGS-B algorithm [57] – an algorithm to perform optimization with bounds on the variables – is used to compute the MS-RPI. A prescription for the initial guess of the nuclear coordinates is provided below:

$$R_{j} = R_{0} + (R_{2} - R_{0})\cos\left(\frac{\pi i}{N_{2} + 3}\right) \quad \text{where } i = 1, \lfloor \frac{N_{2}}{2} \rfloor + 1, j = 1, \lfloor \frac{N_{2}}{2} \rfloor + 1$$

$$R_{\lfloor N_{2}/2 \rfloor + 2} = R_{0} \quad (2.18)$$

$$R_{j} = R_{0} - \left| (R_{0} - R_{1})\cos\left(\frac{\pi}{2} + \frac{\pi i}{N_{1} + 1}\right) \right| \quad \text{where } i = 1, N_{1}, j = \lfloor \frac{N_{2}}{2} \rfloor + 3, \lfloor \frac{N_{2}}{2} \rfloor + N_{1} + 2$$

$$R_{\lfloor N_{2}/2 \rfloor + N_{1} + 3} = R_{0}$$

$$R_{j} = R_{0} + (R_{2} - R_{0})\cos\left(\frac{\pi i}{N_{2} + 3}\right) \quad \text{where } i = \lfloor \frac{N_{2}}{2} \rfloor + 4, N_{2} + 2, j = \lfloor \frac{N_{2}}{2} \rfloor + N_{1} + 4, N$$

Note that in the equations above,  $\lfloor \frac{N}{2} \rfloor$  represents the floor function acting on  $\frac{N}{2}$ . The MV-RPI calculation also requires initial guesses for the electronic coordinates, which are obtained using the nuclear coordinates:

$$[\mathbf{x}_{\alpha}]_n = \sqrt{\frac{e^{-\beta V_{nn}(R_{\alpha})}}{\sum_n e^{-\beta V_{nn}(R_{\alpha})}}}$$
(2.19)

Though the optimization must be independent of the initial guess, a good initial guess speeds up the calculation significantly, as does the inclusion of the gradient of the ring polymer potential in the optimization. Furthermore, to identify the MS-RPI, multiple optimizations are performed with  $N_1$  beads initialized to the left (donor state) and  $N_2$  beads to the right (acceptor state) of the crossing, while two bead constrained to the crossing; the total number of beads of the ring polymer is  $N = N_1 + N_2 + 2$ . The MS-RPI configuration extremizes the corresponding ring polymer potential; in Fig. 2.2, this is demonstrated for the symmetric model system (Model I).



Figure 2.2: The effective mapping variable ring polymer potential energy for a 256-bead ring polymer as a function of the number of beads to the left of the crossing  $(N_1)$ . The system shown here is symmetric model I with  $\beta = 3.25$  a.u. in the nonadiabatic regime,  $\Delta = 0.0077$  a.u. The RPI configurations corresponds to the maximum where  $N_1 = N_2 = 127$  beads (2 beads are fixed at the crossing). Figure has been reproduced from Ref. [45] with permission from the authors.

In order to improve computational efficiency is to follow the algorithm in Fig. 2.3. Here, for each model, the single surface RPI is determined on the lower adiabatic surface. This result serves as the initial guess to the MF-RPI optimization in the adiabatic limit, and that result is, in turn, used as the initial guess for the nuclear coordinates for the MV-RPI optimization. The initial guess for the electronic coordinates are obtained using Eq. 2.19. In all cases, the adiabatic




Figure 2.3: The initial nuclear configuration generated according to Eq. 2.18 is used to find the single surface RPI on the lower adiabatic state. The initial electronic configurations are generated according to Eq. 2.19. The arrows connect initial guess configurations with optimized RPI configurations. Figure has been reproduced from Ref. [45] with permission from the authors.

MS-RPI in the nonadiabatic limit has a larger spread than in the adiabatic limit. This is a consequence of the higher curvature of the barrier in the nonadiabatic limit as shown in Fig. 2.4.

### 2.3.2 Multi-state RPIs for two-state model systems

### The effect of the driving force

The effect of the driving force on the MS-RPI is shown in Fig. 2.5. MV-RPI for models I, II, and III, was converged using 256 beads for the parameters:  $\beta = 3.25$ a.u ,  $\Delta = 0.0077$  a.u.. The number of beads to the left of the crossing increases with the driving force, as shown by the nuclear MV-RPI in Fig. 2.5. The electronic MV-RPI is used to compute the population of the  $n^{\text{th}}$  state in the  $\alpha^{\text{th}}$  bead, via the



Figure 2.4: The adiabatic potential energy surfaces in the adiabatic (black line) and nonadiabatic (red dashed line) coupling limits for model I at  $\beta = 3.25$  a.u. are shown here. A cartoon repsentation of the extent of spread in the nuclear instanton for both the nonadiabatic (red outer ellipse) and adiabatic (black inner ellipse) limits is also shown. Figure has been reproduced from Ref. [45] with permission from the authors.

normalized Wigner population estimator:

$$\mathcal{P}_{\alpha n} = [\mathbf{x}_{\alpha}]_{n}^{2}. \tag{2.20}$$

Table. 2.2 summarizes the key results of the effect of the driving force on the MV-RPI: the ratio  $N_1/N_2$  grows as a function of the driving force, and is seen to be independent of the coupling strength.

### The effect of electronic coupling and temperature

The MV-RPI for model I in the adiabatic ( $\Delta = 6.15$  a.u.) and nonadiabatic ( $\Delta = 0.0077$  a.u.) regimes with  $\beta = 3.25$  a.u. is shown in Fig. 2.6. In keeping with findings from other multistate instanton calculations [36], it was found that the spread of the nonadiabatic nuclear MV-RPI is wider than the corresponding adiabatic MV-RPI. The electronic MV-RPI (donor state populations) are shown to



Figure 2.5: Nuclear bead positions (left) as a function of bead number for model I (red dashed line), model II (green dotted line), and model III (blue dot-dashed line) at  $\beta = 3.25$  a.u. with  $\Delta = 0.0077$  a.u. (nonadiabatic). The horizontal black line indicates the position at which donor and acceptor states cross. Note that bead positions for models II and III have all been shifted by 0.5 a.u. and 1.0 a.u., respectively, so that the crossing of all the three models coincide. The number of beads to the left of the crossing increases as the driving force increases. The associated donor state populations are shown on the right, which are in keeping with the nuclear position changes along the instanton path. Figures have been reproduced from Ref. [45] with permission from the authors.

				A	diabati	ic	Nonadiabatic		
$\epsilon$	$N_1$	$N_2$	$R_0$	$\bar{R}$ $\mathbb{P}_1$ $\mathbb{P}_2$		$\mathbb{P}_2$	R	$\mathbb{P}_1$	$\mathbb{P}_2$
0.0	127	127	0.0	10 <sup>-5</sup>	0.50	0.50	10 <sup>-5</sup>	0.50	0.50
10.0	146	108	-0.5	-0.71	0.57	0.43	-0.74	0.57	0.43
20.0	163	91	-1.0	-1.34	0.63	0.37	-1.45	0.65	0.35

Table 2.2: 256-bead MV-RPI for models I, II and III with  $\beta = 3.25$  a.u. for  $\Delta = 6.15$  a.u. (adiabatic) and  $\Delta = 0.0077$  a.u. (nonadiabatic). The number of beads on the donor  $(N_1)$  and acceptor  $(N_2)$  surfaces excluding the two beads constrained to the crossing is reported along with the position of the nuclear centroid  $(\bar{R})$  and bead-averaged donor and acceptor state populations,  $\mathbb{P}_1$  and  $\mathbb{P}_2$ , respectively. The values of the nuclear variables, and the energies are given in atomic units. Table has been reproduced from Ref. [45] with permission from the authors.

follow the nuclear coordinates, as before. The two beads at the crossing have equal population in the donor and acceptor electronic states in both the adiabatic and nonadiabatic models. However, as shown in the inset, the donor state populations exhibit oscillatory features near the crossing in the adiabatic limit, a feature arising from the use of a diabatic state representation. While the golden-rule instanton places individual beads on one or the other surface [58], the MV-RPI allows for beads with partial populations in keeping with the quantum mechanical probability of the system being in a particular electronic state along the instanton path. Fig. 2.7 shows the effect of temperature on the nuclear MV-RPI. Specifically, for



Figure 2.6: MV-RPI nuclear bead positions as a function of bead number for model I with  $\beta = 3.25$  a.u. and  $\Delta = 6.15$  a.u. (adiabatic, blue line), and  $\Delta = 0.0077$ a.u. (nonadiabatic, red dashed line). The nonadiabatic instanton exhibits a wider spread than the adiabatic instanton in keeping with lower curvature of the barrier in the latter case. The black horizontal line marks the position at which donor and acceptor state diabats cross.electronic MV-RPI donor state populations as a function of bead number for model I with  $\beta = 3.25$  a.u. and  $\Delta = 6.15$  a.u. (adiabatic, blue line), and  $\Delta = 0.0077$  a.u. (nonadiabatic, red dashed line). The inset illustrates electronic state populations vary gradually in the nonadiabatic case but exhibit some oscillatory structure in the adiabatic regime. Figure has been reproduced from Ref. [45] with permission from the authors.

model I with  $\Delta = 0.00625$  a.u.,  $\beta$  is varied from 3.25 a.u. to 4.0 a.u. in steps of 0.25 a.u. The nuclear MV-RPI spread increases as temperature decreases; as the system is cooled, a shift towards deep tunneling with a corresponding increase in the extent of the instanton is expected. The electronic MV-RPI does not change significantly over the range of temperatures considered here.



Figure 2.7: Nucelar bead positions as a function of bead number for a 256bead MV-RPI for model I with  $\Delta = 0.00625$  a.u. (nonadiabatic) and  $\beta = 3.25, 3.5, 3.75, 4.0$  a.u. represented by red dashed, blue continuous, black dotted, and green dot-dashed lines, respectively. The horizontal line is the crossing of the donor and acceptor diabats. Figure has been reproduced from Ref. [45] with permission from the authors.

### Comparison of MF-RPI and MV-RPI

Both the MF and MV formulations are derived from equivalent, exact representations of the quantum canonical partition function; thus, the two nuclear instantons are expected to be nearly indistinguishable as shown in Fig. 2.8.

Although the MF-RPI does not include explicit electronic variables, it is possible to estimate the electronic state populations from the nuclear bead positions along the nuclear instanton path. In keeping with previous work [41], the donor state population of each bead is estimated using the following *ad hoc* expression,

$$\mathbb{P}_{\alpha 1} = \frac{e^{-\beta V_{11}(\mathbf{R}_{\alpha})}}{e^{-\beta V_{11}(\mathbf{R}_{\alpha})} + e^{-\beta V_{22}(\mathbf{R}_{\alpha})}}$$
(2.21)

This MF-RPI result is compared against the electronic MV-RPI populations in Fig. 2.9(a) for nonadiabatic model I with  $\Delta = 0.001$  a.u and  $\beta = 3.25$  a.u.. Examining beads in the vicinity of the crossing, shown in Fig. 2.9(b) and Fig. 2.9(c), it is



Figure 2.8: Nuclear bead positions as a function of bead number for a 256-bead MV-RPI determined for model I at  $\beta = 3.25$  a.u. in the nonadiabatic limit ( $\Delta = 0.0077$  a.u.). The MF-RPI nuclear positions are represented using the blue line while those obtained from the MV-RPI using the red dotted lines. The inset highlights nuclear positions for the first 20 beads where the small numerical difference between the two instantons is most noticeable. Figure has been reproduced from Ref. [45] with permission from the authors.

evident that the populations obtained from the nuclear MF-RPI fail to distinguish between the adiabatic and nonadiabatic regimes over three orders of magnitude. However, the electronic MV-RPI populations show a smooth transition from beads on one state to the other along the instanton path in the nonadiabatic case and an oscillatory structure in the adiabatic case (as expected when working in the diabatic representation). In the adiabatic regime, beads away from the crossing are not fully in one or the other diabatic state in keeping with the underlying model.



Figure 2.9: (a) Comparing donor state populations obtained from the nuclear MF-RPI instanton (blue line with circles) against the electronic MV-RPI populations (red dashed line with triangles) for model I with  $\Delta = 0.001$  a.u. and  $\beta = 3.25$  a.u. (b) Populations for beads in the vicinity of the crossing obtained from the nuclear MF-RPI instanton for model I with  $\beta = 3.25$  a.u. shown for three different coupling strengths,  $\Delta = 6.15$  a.u (red line with squares),  $\Delta = 2.5$  a.u (black dashed line with triangles), and  $\Delta = 0.001$  a.u (blue dot-dashed line with circles). (c) Electronic MV-RPI populations for beads in the vicinity of the crossing for model I with  $\beta = 3.25$  a.u. for three different coupling strengths,  $\Delta = 6.15$  a.u (red line with circles), and  $\Delta = 0.001$  a.u (blue dot-dashed line with circles). (c) Electronic MV-RPI populations for beads in the vicinity of the crossing for model I with  $\beta = 3.25$  a.u. for three different coupling strengths,  $\Delta = 6.15$  a.u (red line with squares),  $\Delta = 2.5$  a.u. (red line with squares),  $\Delta = 2.5$  a.u. (red line with squares),  $\Delta = 2.5$  a.u. (blue dot-dashed line with circles). (c) Electronic MV-RPI populations for beads in the vicinity of the crossing for model I with  $\beta = 3.25$  a.u. (red line with  $\beta = 3.25$  a.u. (red line coupling strengths,  $\Delta = 6.15$  a.u (red line with squares),  $\Delta = 2.5$  a.u. (blue dot-dashed line with circles), and  $\Delta = 0.001$  a.u (blue dot-dashed line with triangles). For comparison, the MF-RPI populations are shown for  $\Delta = 2.5$  a.u. (black dashed line). Figure has been reproduced from Ref. [45] with permission from the authors.

### 2.4 Nonadiabatic reaction rates

The rate constant in the MF framework is the multi-state extension to the RPI rate constant [23, 59, 60]

$$k_{\rm MF-RPI} \approx \frac{2}{\beta} \frac{\mathcal{Z}_b}{\mathcal{Z}_r} = \frac{2e^{-\beta_N V_{\rm MF}(\tilde{\mathbf{R}}_\alpha)}}{\mathcal{Z}_r \beta} \left(\frac{M}{2\pi\beta_N}\right)^{\frac{N}{2}} \int d\{\mathbf{R}_\alpha\} e^{-\beta_{2N} V_{\rm MF}'(\tilde{\mathbf{R}}_\alpha) (\mathbf{R}_\alpha - \tilde{\mathbf{R}}_\alpha)^2}, \quad (2.22)$$

where  $\{\tilde{\mathbf{R}}_{\alpha}\}$  represents the MF-RPI configuration,  $\mathcal{Z}_{b}$  is the barrier partition function,  $\mathcal{Z}_{r}$  is the reactant partition function, and the second derivative  $V_{\text{MF}}^{\prime\prime}$  is evaluated at the MF-RPI configuration. Eq. 2.22 is obtained by expanding the MF-RP potential in a Taylor series evaluated at the MF-RPI solution and truncating to second order. The diagonalization of the hessian  $V_{\text{MF}}^{\prime\prime}(\{\tilde{\mathbf{R}}_{\alpha}\})$  yields N eigenvalues  $(M\lambda_{\alpha}^{2})$ :

$$k_{\rm MF-RPI} = \frac{2e^{-\beta_N V_{\rm MF}(\tilde{\mathbf{R}}_{\alpha})}}{\mathcal{Z}_{r}\beta} \left(\frac{M}{2\pi\beta_N}\right)^{\frac{N}{2}} \int d\{\mathbf{s}_{\alpha}\} e^{-\beta_{2N}\sum_{\alpha}M\lambda_{\alpha}^2 \mathbf{s}_{\alpha}^2}$$
(2.23)

The Hessian evaluated at the MF-RPI configuration yields one negative eigenvalue,  $\lambda_1 < 0$ , and a zero eigenvalue,  $\lambda_2 \approx 0$ , for a bead-converged calculation. The mode  $\mathbf{s}_1$  – corresponding to the negative eigenvalue – is integrated by analytically continuing the Gaussian and performing the integral over the positive part of the imaginary axis; mode  $\mathbf{s}_2$  is integrated out analytically as are the remaining (N-2)Gaussian integrals. The resulting expression for the MF-RPI rate constant is then,

$$k_{\rm MF-RPI} \approx \frac{e^{-\beta_N V_{\rm MF}(\tilde{\mathbf{R}}_{\alpha})}}{\mathcal{Z}_r \beta_N} \left(\frac{M z_N}{2\pi \beta_N}\right)^{\frac{1}{2}} \prod_{\alpha=1}^N \frac{1}{\beta_N |\lambda_{\alpha}|}, \qquad (2.24)$$

where the ' on the product indicates that  $\alpha = 2$  is excluded, and  $z_N = \sum_{\alpha} (\tilde{\mathbf{R}}_{\alpha} - \tilde{\mathbf{R}}_{\alpha+1})^2$ . This expression follows a previously derived nonadiabatic instanton rate, with the primary difference being the method used to find the instanton. [41]

In Fig. 2.10, rate constants for model I, computed as a function of the electronic coupling,  $\Delta$ , are presented. In the nonadiabatic regime, the MF-RPI rate constants



Figure 2.10: MF-RPI rate constants (red circles) as a function of the coupling strength for model I at  $\beta = 4.0$  a.u. In the nonadiabatic regime, there is good agreement with the FGR rate constants (dashed black line) and in the adiabatic regime, MF-RPI results are within a factor of 2 of the single surface RPI rate constants (blue line). Figure has been reproduced from Ref. [45] with permission from the authors.

Δ	$\log_{10} k_{\rm MF-RPI}$	$\log_{10} k_{\rm FGR}$	$\log_{10} k_{RP}$
0.01	-37.398	-37.395	-
0.1	-35.397	-35.395	-
0.25	-34.598	-34.599	-
1.0	-33.327	-33.395	-32.182
2.5	-32.153	-32.599	-31.628
5.0	-30.269	-31.997	-29.966
10.0	-24.836	-31.395	-24.444

Table 2.3: Comparing rate constants for model I at  $\beta = 4.0$  a.u. with different coupling strengths.  $k_{\text{MF-RPI}}$  is the MF-RPI rate constant,  $k_{\text{FGR}}$  is the rate constant obtained using Fermi's Golden Rule, and  $k_{\text{RP}}$  is the rate constant computed using single surface RPI determined on the lower adiabatic surface. Note that  $k_{\text{RP}}$  is only calculated for cases where the RPI has a numerical zero mode. Table has been reproduced from Ref. [45] with permission from the authors.

Model	$\epsilon$	$\log_{10} k_{\rm MF-RPI}$	$\log_{10} k_{\rm FGR}$		
Ι	0.0	-37.805	-37.803		
II	10.0	-29.913	-29.913		
III	20.0	-23.485	-23.508		

Table 2.4: MF-RPI rates compared with FGR rates for nonadiabatic models I, II and III with  $\beta = 4.0$  a.u.,  $\Delta = 0.0625$  a.u. Table has been reproduced from Ref. [45] with permission from the authors.

are in good agreement with Fermi's Golden Rule (FGR) rate constants. In the adiabatic regime the rate constant is computed using the single surface RPI on the lower adiabatic surface; they agree well with the MF-RPI rates, as reported in Table 2.3. In the intermediate coupling regime, the MF-RPI rate expression interpolates smoothly and accurately between the nonadiabatic and adiabatic coupling regimes. The agreement between the MF-RPI and FGR rates for models I, II, and III in the nonadiabatic regime with  $\Delta = 0.0625$  a.u. where driving force is varied is found to be good, and is reported in Table 2.4.

### CHAPTER 3

## THE COMPUTATION OF CONDENSED PHASE REACTION RATES

The computation of condensed phase reaction rates has been of interest to the chemistry community. Classical and quantum rate theories have been developed, which build on Kramers' theory [61]. The connection between the generalized Langevin equations and the Hamiltonian with linear system-bath coupling was established by Zwanzig [62]. Canonical quantization extends the same Hamiltonian to the study of dissipative quantum systems. The rate of tunneling from a metastable state was obtained using the instanton method within the influence functional formulation [11]; it was concluded that dissipation suppressed QM tunneling [63]. In this chapter, the dissipative tunneling problem is formulated using RPs for the system-bath Hamiltonian of both adiabatic and multi-state quantum systems. Reduced dimensional RP formulations are obtained for both the adiabatic and multi-state systems, by integrating out the bath degrees of freedom in the normal mode representation; the computed dissipative tunneling rates are in keeping with the expectation that tunneling rates decrease with increasing system-bath coupling.

### 3.1 Single surface system-bath Hamiltonians

In general, a system-bath Hamiltonian is made up of three terms – the system Hamiltonian,  $\hat{H}_s$ ; the Hamiltonian for the bath dofs,  $\hat{H}_b$ ; and the system-bath interaction Hamiltonian,  $\hat{H}_{sb}$ :

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb} \quad \text{where,} \tag{3.1}$$

$$\hat{H}_{s}(\hat{r},\hat{p}) = \frac{\hat{p}^{2}}{2M} + V(\hat{r}) + \sum_{k=1}^{f} \frac{c_{k}^{2}}{2M_{b}\omega_{k}^{2}} \hat{r}^{2}$$
(3.2)

$$\hat{H}_{b}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) = \sum_{k=1}^{f} \left[ \frac{\hat{P}_{k}^{2}}{2M_{b}} + \frac{M_{b}\omega_{k}^{2}\hat{R}_{k}^{2}}{2} \right]$$
(3.3)

$$\hat{H}_{sb}(\hat{r}, \hat{\mathbf{R}}) = \sum_{k=1}^{J} c_k \hat{R}_k \hat{r}$$
(3.4)

where  $\hat{r}$ ,  $\hat{p}$ , M represent the positions, momenta, and mass of the system dof;  $\hat{P}_k, \hat{R}_k, M_b$  represent the position, momentum and mass of the  $k^{\text{th}}$  bath dof;  $\omega_k$  is its frequency and  $c_k$ , its coupling to the system dof. The spectral density of the bath is Ohmic,

$$J(\omega) = \eta \omega e^{-\omega/\omega_c}, \qquad (3.5)$$

where  $\omega_c$  is the cutoff frequency and  $\eta$  is the friction coefficient. The continuous spectral density is discretized using f quantum harmonic oscillators:

$$J(\omega) = \frac{\pi}{2} \sum_{k=1}^{f} \frac{c_k^2}{M_b \omega_k} \delta(\omega - \omega_k)$$
(3.6)

with frequencies  $\omega_k$  and coupling  $c_k$ :

$$\omega_k = -\omega_c \log_{10} \left( \frac{k - 0.5}{f} \right), \tag{3.7}$$

$$c_k = -\omega_k \left(\frac{2\eta M \omega_c}{f\pi}\right)^{1/2}.$$
 (3.8)

For simplicity of presentation, the system dof is assumed to be one dimensional; extension to the case of a multidimensional system is straightforward.

### 3.1.1 System-bath ring polymers

The canonical partition function,  $\mathcal{Z}$ , is obtained by evaluating the trace, now over both the system and bath dofs, of the Boltzmann operator using a mixed-time splitting:

$$\mathcal{Z}_{sb} = \operatorname{Tr}_{sb} \left[ e^{-\beta \hat{H}} \right] \tag{3.9}$$

$$= \operatorname{Tr}_{sb}\left[\left(\left\{e^{-\beta_{s}[\hat{H}_{s}+\hat{H}_{sb}]}\right\}^{N_{s}/N_{b}}e^{-\beta_{b}\hat{H}_{b}}\right)^{N_{b}}\right].$$
(3.10)

where  $N_s$  and  $N_b$  are the number of imaginary time slices (beads) corresponding to the system and bath dofs, respectively, with  $N_s \ge N_b$ , and  $\beta_s \equiv \beta/N_s$ ,  $\beta_b \equiv \beta/N_b$ . The trace is evaluated in the position basis by the introduction of  $N_s$  and  $N_b$ resolutions of identity:

$$\mathbb{1}_{s} = \int dr |r\rangle \langle r|, \qquad (3.11)$$

$$\mathbb{1}_{b} = \int d\mathbf{R} |\mathbf{R}\rangle \langle \mathbf{R}|, \qquad (3.12)$$

in the system and bath dofs, respectively. The resulting configurational integral for  $\mathcal{Z}$  is:

$$\mathcal{Z}_{sb} = \lim_{N_s, N_b \to \infty} \mathcal{A}_{sb} \int d\{r_\alpha\} \int d\{\mathbf{R}_\gamma\} e^{-\beta V_{sb}(\{r_\alpha\}, \{\mathbf{R}_\gamma\})}.$$
 (3.13)

The premultiplicative constant is:

$$\mathcal{A}_{sb} = \left(\frac{MN_s}{2\pi\beta}\right)^{N_s/2} \left(\frac{M_b N_b}{2\pi\beta}\right)^{fN_b/2}, \qquad (3.14)$$

and the full dimensional system-bath ring polymer potential is:

$$V_{sb} = \mathcal{U}_s + \mathcal{U}_b + \mathcal{U}_{sb}. \tag{3.15}$$

The contributions to  $V_{sb}$  can be separated as system, bath, and system-bath coupling terms:

$$\mathcal{U}_{s} = \sum_{\alpha=1}^{N_{s}} \left[ \frac{M \left( r_{\alpha} - r_{\alpha+1} \right)^{2}}{2\beta_{s}^{2} N_{s}} + \frac{V(r_{\alpha})}{N_{s}} + \sum_{k=1}^{f} \frac{c_{k}^{2} r_{\alpha}^{2}}{2M_{b} \omega_{k}^{2} N_{s}} \right],$$
(3.16)

$$\mathcal{U}_{b} = \sum_{\gamma=1}^{N_{b}} \sum_{k=1}^{f} \left[ \frac{M_{b} \omega_{k}^{2} R_{\gamma,k}^{2}}{2N_{b}} + \frac{M_{b} (R_{\gamma,k} - R_{\gamma+1,k})^{2}}{2\beta_{b}^{2} N_{b}} \right], \qquad (3.17)$$

$$\mathcal{U}_{sb} = \frac{1}{N_s} \sum_{k=1}^f \sum_{\gamma=1}^{N_b} \sum_{\mu=1}^{N_s/N_b} c_k R_{\gamma,k} r_{(\gamma-1)\frac{N_s}{N_b}+\mu}.$$
(3.18)

This is an exact expression for the canonical partition function, in the limit that  $N_s$ and  $N_b$  – the number of system and bath beads – go to infinity. When performing numerical calculations,  $N_s$  and  $N_b$  must be chosen such that the ratio  $N_s/N_b$  is an integer.

### 3.1.2 Reduced dimensional ring polymers

The description of the bath using QHOs allows for the formulation of a reduced dimensional representation of the system, where the partition function is written as a configurational integral of the reduced dimensional ring polymer potential which is dependent on the system bead coordinates alone. In Eq. 3.15,  $N_b$  and  $N_s$  are both set to N, i.e., the number of beads of the system and bath ring polymers is the same. This is followed by a transformation from the ring polymer bead representation  $(\mathbf{\tilde{r}})$  using the transformation matrix  $\mathbf{C}$ :

$$\tilde{\mathbf{r}} = \mathbf{C}^T \mathbf{r},\tag{3.19}$$

whose matrix elements  $C_{\alpha\nu}$  are given by:

$$C_{\alpha\nu} = \sqrt{\frac{1}{N}}, \qquad \nu = 0$$
  
$$= \sqrt{\frac{2}{N}} \cos\left(\frac{2\pi\alpha\nu}{N}\right), \qquad 1 \le \nu \le \frac{N}{2} - 1$$
  
$$= \sqrt{\frac{1}{N}}(-1)^{\alpha}, \qquad \nu = \frac{N}{2}$$
  
$$= \sqrt{\frac{2}{N}} \sin\left(\frac{2\pi\alpha\nu}{N}\right), \qquad \frac{N}{2} + 1 \le \nu \le N - 1 \qquad (3.20)$$

where  $\alpha = 1, ..., N$  and  $\nu = 0, ..., N - 1$ , and the frequency of the  $\nu^{\text{th}}$  ring polymer normal mode is:

$$\omega_{\nu} = \frac{2}{\beta_N} \sin\left(\frac{\nu\pi}{N}\right). \tag{3.21}$$

The completion of squares in the normal mode representation yields:

$$\widetilde{V}_{sb} = \sum_{\nu=0}^{N-1} \left[ \frac{M\omega_{\nu}^{2}\widetilde{r}_{\nu}^{2}}{2N} + \frac{V(\widetilde{r}_{\nu})}{N} + \sum_{k=1}^{f} \frac{c_{k}^{2}\widetilde{r}_{\nu}^{2}}{2M_{b}\omega_{k}^{2}N} \right] - \sum_{\nu=0}^{N-1} \sum_{k=1}^{f} \frac{c_{k}^{2}\widetilde{r}_{\nu}^{2}}{2M_{b}(\omega_{\nu}^{2} + \omega_{k}^{2})N} \\
+ \sum_{\nu=0}^{N-1} \sum_{k=1}^{f} \frac{M_{b}(\omega_{\nu}^{2} + \omega_{k}^{2})}{2N} \left\{ \widetilde{R}_{k,\nu} + \frac{c_{k}\widetilde{r}_{\nu}}{M_{b}(\omega_{\nu}^{2} + \omega_{k}^{2})} \right\}^{2}.$$
(3.22)

Here,  $\omega_{\nu}$  is the frequency of the  $\nu^{\text{th}}$  normal mode,  $\tilde{r}_{\nu}$  and  $\tilde{R}_{k,\nu}$  are the positions of the system and bath beads in the normal mode coordinates. The bath variables

in Eq. 3.22 can be integrated analytically using properties of gaussian integrals. The resulting reduced dimensional potential is transformed back into the bead representation:

$$V_{\text{red}}(\{r_{\alpha}\}) = \sum_{\alpha=1}^{N} \left[ \frac{M(r_{\alpha} - r_{\alpha+1})^2}{2\beta_s^2 N} + \frac{V(r_{\alpha})}{N} + \sum_{k=1}^{f} \frac{c_k^2 r_{\alpha}^2}{2M_b \omega_k^2 N} \right] - \sum_{\alpha,\gamma=1}^{N} r_{\alpha} \left( \sum_{\nu=0}^{N-1} \sum_{k=1}^{f} \frac{c_k^2 C_{\alpha\nu} C_{\nu\gamma}}{2M_b (\omega_{\nu}^2 + \omega_k^2) N} \right) r_{\gamma}$$
(3.23)

where  $C_{\alpha\gamma}$  are elements of the transformation matrix. The effect of the bath dofs on the system dof is encapsulated in the last term (Eq. 3.23). The integration over the bath variables modifies the premultiplicative constants as follows:

$$\mathcal{A}_{b} = \prod_{\nu=0}^{N-1} \prod_{k=1}^{f} \left( \frac{2\pi N}{M_{b}\beta(\omega_{f}^{2} + \omega_{\nu}^{2})} \right)^{1/2}$$

$$\mathcal{A}_{s} = \mathcal{A}_{sb} \times \mathcal{A}_{b}$$

$$(3.24)$$

$$= \left(\frac{MN}{2\pi\beta}\right)^{N/2} \prod_{\nu=0}^{N-1} \prod_{k=1}^{f} \frac{1}{\beta_N \sqrt{\omega_k^2 + \omega_\nu^2}}$$
(3.25)

The canonical partition function in the reduced representation is:

$$\mathcal{Z}_{\text{red}} = \lim_{N_s \to \infty} \mathcal{A}_s \int d\{r_\alpha\} e^{-\beta V_{\text{red}}(\{r_\alpha\})}.$$
(3.26)

### 3.2 Multi-state system-bath Hamiltonians

Akin to the Hamiltonian described in Eq. 3.1 for a single surface reaction, a multistate system coupled to a bath can be described using the following Hamiltonian:

$$\hat{H}_{\rm MS} = \hat{H}_{\rm MS,s} + \hat{H}_b + \hat{H}_{sb} \tag{3.27}$$

$$\hat{H}_{MS,s}(\hat{r},\hat{p}) = \frac{\hat{p}^2}{2M} + \sum_{n,m=1}^{N} |\psi_n\rangle V(\hat{r})\langle\psi_m|$$
 (3.28)

$$\hat{H}_{b}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) = \sum_{k=1}^{f} \left[ \frac{\hat{P}_{k}^{2}}{2M_{b}} + \frac{M_{b}\omega_{k}^{2}\hat{R}_{k}^{2}}{2} \right]$$
(3.29)

$$\hat{H}_{sb}(\hat{r}, \hat{\mathbf{R}}) = \sum_{k=1}^{f} c_k \hat{R}_k \hat{r}$$
(3.30)

where  $\hat{r}$  and  $\hat{p}$  represent the positions and momenta of the nuclear dof;  $|\psi_n\rangle$  is the  $n^{\text{th}}$  diabatic state.  $\hat{P}_k, \hat{R}_k, \omega_k, c_k$  represent the position, momentum, frequency and coupling to the nuclear dof of the  $k^{\text{th}}$  bath dof; the external bath is modeled as a collection of quantum harmonic oscillators.

### 3.2.1 System-bath multi-state ring polymers

The canonical partition function, Z, is obtained by evaluating the trace – now over both the nuclear, electronic, and bath dofs; indicated by the subscript *neb* – of the Boltzmann operator using a mixed-time splitting procedure:

$$\mathcal{Z} = \operatorname{Tr}_{neb}\left[e^{-\beta\hat{H}_{\mathrm{MS}}}\right] = \operatorname{Tr}_{neb}\left[\left(\left\{e^{-\beta_{s}\left[\hat{H}_{\mathrm{MS},s}+\hat{H}_{sb}\right]}\right\}^{N_{s}/N_{b}}e^{-\beta_{b}\hat{H}_{b}}\right)^{N_{b}}\right], \quad (3.31)$$

where  $N_s$  and  $N_b$  are the number of imaginary time slices (beads) corresponding to the system and bath dofs, respectively, with  $N_s \ge N_b$ , and  $\beta_s \equiv \beta/N_s$ ,  $\beta_b \equiv \beta/N_b$ . The trace over the nuclear and bath dofs is evaluated in the position basis; and, as before, the trace in the electronic dofs can be evaluated in a number of ways, resulting in different representations of  $\mathcal{Z}$ . The MF and MV partition functions are provided below.

### Mean Field Partition Function

Here, the trace over the system coordinates can be evaluated using the following completeness relation:

$$\mathbb{1}_{ne} = \int dr |r\rangle \langle r|\mathcal{P} \text{ where,} \qquad (3.32)$$

$$\mathcal{P} = \sum_{n=1}^{\mathcal{K}} |\psi_n\rangle \langle \psi_n| \qquad (3.33)$$

is the completeness relation in the diabatic state basis. Thus, the partition function for the mean-field case is:

$$\begin{aligned} \mathcal{Z}_{MF,sb} &= \lim_{N_{s},N_{b}\to\infty} \mathcal{A}_{sb} \int d\{\mathbf{R}_{\gamma}\} \int d\{r_{\alpha}\} e^{-\beta V_{MF,sb}} \operatorname{sgn}(\Gamma_{MF,sb}) \quad (3.34) \\ V_{MF,sb} &= \sum_{k=1}^{f} \sum_{\gamma=1}^{N_{b}} \left( \frac{M_{b} \omega_{k}^{2} R_{\gamma,k}^{2}}{2N_{b}} + \frac{M_{b} (R_{\gamma,k} - R_{\gamma+1,k})^{2}}{2\beta_{b}^{2} N_{b}} \right) \\ &+ \sum_{\alpha=1}^{N_{s}} \left[ \frac{M (r_{\alpha} - r_{\alpha+1})^{2}}{2\beta_{s}^{2} N_{s}} + \sum_{k=1}^{f} \frac{c_{k}^{2} r_{\alpha}^{2}}{2N_{s} M_{b} \omega_{k}^{2}} \right] - \frac{1}{\beta} \ln |\Gamma_{MF,sb}| \quad (3.35) \end{aligned}$$

and 
$$\mathcal{A}_{sb} = \left(\frac{MN_s}{2\pi\beta}\right)^{N_s/2} \left(\frac{M_bN_b}{2\pi\beta}\right)^{fN_b/2}$$
. (3.36)

Here,

$$\Gamma_{\mathrm{MF},sb} = \mathrm{Tr}\left[\prod_{\gamma=1}^{N_b} \left\{\prod_{\mu=1}^{\frac{N_s}{N_b}} \mathcal{M}\left(\mathbf{R}_{\gamma}; r_{(\gamma-1)\frac{N_s}{N_b}+\mu}\right)\right\}\right],\tag{3.37}$$

and,  $\mathbf{R}_{\gamma} \equiv \{R_{\gamma,1}, R_{\gamma,2}, \dots, R_{\gamma,f}\}$  – the coordinates of the  $\gamma^{\text{th}}$  bead for the f bath QHOs; the matrix elements of  $\mathcal{M}(\mathbf{R}_{\gamma}; r)$  are:

$$\mathcal{M}_{nn} = \exp\left[-\beta_s \left(V_{nn}(r) + \sum_{k=1}^f c_k R_{\gamma,k} r\right)\right]$$
$$\mathcal{M}_{nm} = -\beta_s V_{nm}(r) \mathcal{M}_{nn} \quad \text{for } n \neq m \qquad (3.38)$$

### Mapping Variable Partition Function

Continuous variables for the electronic dofs can be introduced using the Stock-Thoss mapping protocol described in Sec. 2.1.2 using the following completeness relation:

$$\mathbb{1}_{ne} = \int dr \, d\mathbf{x} \, |r \, \mathbf{x}\rangle \langle r \, \mathbf{x}| \, \mathcal{P} \quad \text{where,} \qquad (3.39)$$

$$\mathcal{P} = \sum_{n=1}^{\mathcal{K}} |n\rangle \langle n| \qquad (3.40)$$

is the completeness relation in the SEO space. The mapping variable representation of the canonical partition function for the multi-state system-bath Hamiltonian is given by:

$$\mathcal{Z}_{\mathrm{MV},sb} = \lim_{N_{s},N_{b}\to\infty} \mathcal{A}_{sb} \int d\{\mathbf{R}_{\gamma}\} \int d\{r_{\alpha}\} \int d\{\mathbf{x}_{\alpha}\} e^{-\beta V_{\mathrm{MV},sb}} \mathrm{sgn}(\Gamma_{\mathrm{MV}})$$

$$V_{\mathrm{MV},sb} = \sum_{k=1}^{f} \sum_{j=1}^{N_{b}} \left(\frac{M_{b}\omega_{k}^{2}\mathbf{R}_{\gamma,k}^{2}}{2N_{b}} + \frac{M_{b}(\mathbf{R}_{\gamma,k} - \mathbf{R}_{\gamma+1,k})^{2}}{2\beta_{b}^{2}N_{b}}\right) + \frac{1}{\beta} \sum_{\alpha=1}^{N_{s}} \sum_{n=1}^{\mathcal{K}} \mathbf{x}_{\alpha,n}^{2}$$

$$+ \sum_{\alpha=1}^{N_{s}} \left[\frac{M(r_{\alpha} - r_{\alpha+1})^{2}}{2\beta_{s}^{2}N_{s}} + \sum_{k=1}^{f} \frac{c_{k}^{2}r_{\alpha}^{2}}{2N_{s}M_{b}\omega_{k}^{2}}\right] - \frac{1}{\beta}\ln|\Gamma_{\mathrm{MV},sb}| \qquad (3.41)$$

$$\mathcal{A}_{\mathrm{MV},sb} = \mathcal{A}_{sb} \times \left(\frac{2M}{\beta_{s}\pi^{\mathcal{K}+1}}\right)^{\frac{N_{s}}{2}}$$

where the  $\Gamma_{MV}$  is given by:

$$\Gamma_{\mathrm{MV},sb} = \mathrm{Tr}\left[\prod_{\gamma=1}^{N_b} \left\{ \prod_{\mu=1}^{\frac{N_s}{N_b}} \mathcal{X}_{(\gamma-1)\frac{N_s}{N_b}+\mu} \mathcal{M}\left(\mathbf{R}_{\gamma}; r_{(\gamma-1)\frac{N_s}{N_b}+\mu}\right) \right\} \right].$$
(3.42)

The elements of the  $\mathcal{M}(\mathbf{R}_{\gamma}; r)$  matrix are as given in Eq. 3.38 and  $\mathcal{X}_{\mu} = \mathbf{x}_{\mu} \otimes \mathbf{x}_{\mu}^{T}$ .

### 3.2.2 Reduced dimensional multi-state ring polymers

Beginning with Eqs. 3.35 and 3.41 and following the procedure outlined in Sec. 3.1.2, the reduced dimensional representations of the canonical partition for the multi-state systems in the MF and MV formulations, can be determined. Following the previous derivation, final expressions for  $\mathcal{Z}_{MF,red}$  – the reduced dimensional MF partition function, and  $\mathcal{Z}_{MV,red}$  – the reduced mapping variable partition function, are derived.

### Reduced dimensional mean field ring polymers

The canonical partition function is expressed as an integral over just the nuclear bead coordinates:

$$\mathcal{Z}_{\mathrm{MF,red}} = \lim_{N_s \to \infty} \mathcal{A}_s \int d\{r_\alpha\} e^{-\beta \mathrm{V}_{\mathrm{MF,red}}(\{r_\alpha\})} \mathrm{sgn}(\Gamma_{\mathrm{MF,red}}), \qquad (3.43)$$

and the reduced dimensional mean field potential is:

$$V_{\rm MF,red}(\{r_{\alpha}\}) = \sum_{\alpha=1}^{N} \left[ \frac{M(r_{\alpha} - r_{\alpha+1})^2}{2\beta_s^2 N} + \sum_{k=1}^{f} \frac{c_k^2 r_{\alpha}^2}{2M_b \omega_k^2 N} \right] \\ - \sum_{\alpha,\gamma=1}^{N} r_{\alpha} \left( \sum_{\nu=0}^{N-1} \sum_{k=1}^{f} \frac{c_k^2 C_{\alpha\nu} C_{\nu\gamma}}{2M_b (\omega_{\nu}^2 + \omega_k^2) N} \right) r_{\gamma} - \frac{1}{\beta} \ln |\Gamma_{\rm MF,red}|. \quad (3.44)$$

It is to be noted that in this formulation, the asymmetric Trotter splitting is used, the matrix elements of  $\mathcal{M}(r)$  are, now, given by:

$$\mathcal{M}_{nn}(r) = e^{-\beta_s V_{nn}(r)}, \qquad \mathcal{M}_{nm}(r) = -\beta_s V_{nm}(r) \mathcal{M}_{nn}(r) \qquad (3.45)$$

### Reduced dimensional mapping variable ring polymers

Upon integration of the bath dofs, the reduced dimensional canonical partition function can be written as an integral over the continuous nuclear and electronic variables:

$$\mathcal{Z}_{\mathrm{MV,red}} = \lim_{N_s \to \infty} \mathcal{A}_{\mathrm{MV,red}} \int d\{r_{\alpha}\} \int d\{\mathbf{x}_{\alpha}\} e^{-\beta V_{\mathrm{MV,red}}(\{r_{\alpha}\},\{\mathbf{x}_{\alpha}\})} \mathrm{sgn}(\Gamma_{\mathrm{MV,red}}), \quad (3.46)$$

giving us the effective MV ring polymer potential:

$$V_{\text{MV,red}}(\{r_{\alpha}\}) = \sum_{\alpha=1}^{N} \left[ \frac{M(r_{\alpha} - r_{\alpha+1})^{2}}{2\beta_{s}^{2}N} + \sum_{k=1}^{f} \frac{c_{k}^{2}r_{\alpha}^{2}}{2M_{b}\omega_{k}^{2}N} \right] + \frac{1}{\beta} \sum_{\alpha=1}^{N} \sum_{n=1}^{\mathcal{K}} \mathbf{x}_{\alpha,n}^{2} - \sum_{\alpha,\gamma=1}^{N} r_{\alpha} \left( \sum_{\nu=0}^{N-1} \sum_{k=1}^{f} \frac{c_{k}^{2}C_{\alpha\nu}C_{\nu\gamma}}{2M_{b}(\omega_{\nu}^{2} + \omega_{k}^{2})N} \right) r_{\gamma} - \frac{1}{\beta} \ln |\Gamma_{\text{MV,red}}| \quad (3.47)$$

where

$$\Gamma_{\rm MV,red} = \operatorname{Tr}\left[\prod_{\alpha=1}^{N} \mathcal{X}_{\alpha} \mathcal{M}(r_{\alpha})\right],\tag{3.48}$$

and  $X_{\alpha} = \mathbf{x}_{\alpha} \otimes \mathbf{x}_{\alpha}^{T}$ , as defined before.

### **3.3** Rate constants in the condense phase

# 3.3.1 Reduced dimensional formulation of the system-bath rate

The rate expressions for both the reduced dimensional (RD) single surface and multi-state partition functions are obtained using a procedure similar to the one in Sec. 2.4; thus, only the final expressions provided here. The single surface rate constant is:

$$k_{\rm red} \approx \frac{2}{\beta} \frac{Z_{\rm red,b}}{Z_{\rm red,r}}$$
 (3.49)

where  $Z_{\text{red},b}$  and  $Z_{\text{red},r}$  are the RD barrier and reactant partition functions. The barrier partition function is written in terms of the reduced RPI and the eigenvalues of the Hessian computed at the RPI configuration:

$$\mathcal{Z}_{b} = \frac{N\sqrt{z_{N}}\mathcal{A}_{s}}{2}e^{-\beta_{N}V_{sb}(\bar{r}_{\alpha})}\left(\frac{2\pi}{M\beta_{N}}\right)^{\frac{N-1}{2}}\prod_{\alpha=1}^{N} \frac{1}{|\lambda_{\alpha}|}, \qquad (3.50)$$

where  $\{\lambda_{\alpha}\}$  are the eigenvalues of the hessian obtained from Eq. 3.23. The rate constant is given by:

$$k_{\text{red}} = \prod_{\nu=0}^{N-1} \prod_{k=1}^{f} \frac{1}{\beta_N \sqrt{\omega_k^2 + \omega_\nu^2}} \times \frac{1}{\beta_N \mathcal{Z}_r} \sqrt{\frac{M z_N}{2\pi \beta_N}} e^{-\beta_N V_{\text{red}}(\bar{r}_\alpha)} \prod_{\alpha=1}^{N} \frac{1}{\beta_N |\lambda_\alpha|} \quad (3.51)$$

where the ' indicates that the zero mode has been analytically integrated out. The negative eigenvalue mode is integrated over the positive half of the imaginary axis, by analytic continuation. The reactant partition function is:

$$\mathcal{Z}_r = \frac{1}{2\sinh\left(\frac{\beta\omega}{2}\right)} \prod_{k=1}^f \frac{1}{2\sinh\left(\frac{\beta\omega_k}{2}\right)},$$
(3.52)

where it is assumed the reactant well is harmonic with frequency  $\omega$ .

## 3.3.2 Reduced dimensional mean-field formulation of the rate

Following the derivation outlined in Sec. 3.3.1, the rate constant expression for multi-state systems in the condensed phase can be obtained. It only differs from Eq. 3.51, in the ring polymer potential used; the eigenvalues are, accordingly, obtained by diagonalizing the Hessian derived from Eq. 3.44.

$$k_{\rm MF,red} = \prod_{\nu=0}^{N-1} \prod_{k=1}^{f} \frac{1}{\beta_N \sqrt{\omega_k^2 + \omega_\nu^2}} \times \frac{1}{\beta_N \mathcal{Z}_r} \sqrt{\frac{M z_N}{2\pi\beta_N}} e^{-\beta_N V_{\rm MF,red}(\bar{r}_\alpha)} \prod_{\alpha=1}^{N} \frac{1}{\beta_N |\lambda_\alpha|} (3.53)$$

### 3.4 Model systems

### **3.4.1** Adiabatic condensed phase model

The double well system coupled to an Ohmic bath (DW1), modeling proton tunneling, serves as a good test case for the reduced dimensional RPI method [64]:

$$V(x) = -\frac{m\omega_b^2}{2}x^2 + \frac{m^2\omega_b^4}{16E_b}x^4 + E_b.$$
 (3.54)

It is coupled an external bath modeled using harmonic oscillators. The parameters for the double well are given in Table 3.1. Here,  $E_b$  is the barrier height;  $\omega_b$ , the

	$E_b$	$\omega_b$	$\omega_0$	$\omega_c$
DW1	2085	500	707	500

Table 3.1: Parameters of the double well potential. Values are in units of  $cm^{-1}$ 

frequency of the barrier;  $\omega_0$ , the frequency of the reactant well; and  $\omega_c$  is the cutoff frequency for the bath. All the parameters are given in  $cm^{-1}$ .

### 3.4.2 Nonadiabatic condensed phase model

Proton tunneling modeled using a system with two diabatic states coupled to a dissipative bath is considered. The diabatic surfaces are assumed to be harmonic with frequency  $\omega_0$ , constant electronic coupling  $\Delta$  and driving force  $\Delta V$ . The mass of the proton coordinate is  $m_0 = 1836$  a.u. The parameters are provided in Table. 3.2

$\omega_0$	$E_b$	Δ	$\Delta V$	
500	1500	50	0	

Table 3.2: Parameters of the dissipative nonadiabatic proton tunneling model. Values are in units of  $cm^{-1}$ 



Figure 3.1: Adiabatic proton transfer model (left) described in Ref. [65] – a double well potential coupled to a bath; nonadiabatic (right) proton transfer model described in Ref. [64] describing the transfer of a proton from a donor (red) to acceptor (blue).

### 3.5 Simulation details

The numerical determination of the RPI requires an initial guess. For the system DoF, the procedure outlined in Sec. 2.3.1 is followed here, and for the full system-bath RPI calculations, the bath beads are initialized for each bath mode are initialized using:

$$x_{\text{bath},\alpha} = \sin\left(\frac{2\pi\alpha}{N_b}\right) \quad \alpha = 1, 2, \dots, N_b.$$
 (3.55)

The system bath RPIs are obtained by determining the first order saddle point on the extended RP potentials given by Eq. 3.18 – for the adiabatic system; and, Eqs. 3.35 and 3.41 for the multi-state system. Similarly, the reduced dimensional RPIs are obtained by solving Eq. 3.23, and Eqs. 3.44 and 3.47 for the adiabatic, and multi-state systems, respectively. In all calculations, the L-BFGS-B algorithm is used, as before.

### 3.6 Results and discussion

## 3.6.1 Adiabatic system-bath and reduced dimensional RPIs

System-bath RPIs (sbRPIs) and reduced dimensional RPIs (rRPIs) were determined for the double well model system described by Eq. 3.54, for dimensionless friction values  $\eta/M\omega_b = 0.05, 0.1$  at T = 50, 75, 100 K. The crossover temperature  $T_c \approx 114K$ ; thus, QM tunneling is observed for all the temperatures studied here. Fig. 3.2 compares the rRPI and sbRPI at high (50 K) and low (100 K) temperatures; 256 beads were used for the system DoF in both cases, while 32 beads were used for each bath mode in the sbRPI calculation; the rRPI is shown as a continuous black line and the sbRPI is plotted using red dots. They agree exactly with each other at low temperatures, but at high temperature the rRPI predicts a smaller spread than the sbRPI.



Figure 3.2: Plots comparing the rRPI (continuous black line) and the system sbRPI (red dots) at 50 K (left) and 100 K (right), for the dimensionless friction value of  $\eta/M\omega_b = 0.05$ ; 256 beads were used for the determination of the rRPI, and the system DoF in sbRPI, while 32 beads were used for each bath RP in the sbRPI calculation.

The proton tunneling DoF is plotted in Fig. 3.3 for the cases where it interacts with a classical and quantum bath; 1 bead and 32 beads are used to represent each bath DoF, respectively. The sbRPI has a larger spread in the latter case; this is because: the RP beads of a quantum bath DoF has a finite spread and can take up energy from the system DoF thereby reducing the population of higher vibrational levels in the donor and acceptor wells, thereby increasing the spread of the sbRPI which connects lower vibrational states.

The effect of the variation of dimensionless friction and the temperature on the reduced dimensional RPI is shown in Fig. 3.4. The results are in keeping with expectations: at lower temperatures, only the low-lying vibrational states are populated resulting in a larger spread for the rRPI; and, in the weak system-



Figure 3.3: The system sbRPI determined at 50K and  $\eta/M\omega_b = 0.05$  for a quantum (continuous black line) and classical (red dots) bath. 256 beads were used to represent the system RP, whereas 32 beads were used for each bath DoF in the quantum limit, and 1 bead was used in the classical limit.

bath coupling regime considered here, the spread of the rRPI increases due to the reduction in the population of the higher vibrational levels.

The rRPI can be used to determine the rate using Eq. 3.51. The reduced dimensional rate constant  $k_{\rm red}$  is compared with benchmark QUAPI rate constants  $k_{\rm QUAPI}$  for the model system in Table. 3.3. They agree with each other to within a factor of 3 or 4, indicating that the rRPI approximation can be used reliably to compute reaction rates at temperatures below the crossover temperature of the system. The classical rate constants, computed using the expression:

$$k_{cl} = \frac{\omega_0}{2\pi} e^{-\beta E_b},\tag{3.56}$$

are also tabulated, to emphasize that QM tunneling effects are important at low



Figure 3.4: A comparison of the rRPI for  $\eta/M\omega_b = 0, 0.05, 0.1$  (blue, red) and RPI (black) for the system DoF ( $\eta/M\omega_b = 0$ ) at T = 50 K is shown on the left; the rRPIs determined for the adiabatic model with  $\eta/M\omega_b = 0.05$  at a temperature of 100 K (black), 75 K (blue), and 50 K (red), is shown on the right; 256 beads are used to represent the RP in both cases. The bead positions  $x_{\alpha}$  are in a.u.

η	Т	$N_s$	$\log_{10} k_{\text{QUAPI}}$	$\log_{10} k_{\rm red}$	$\log_{10} k_{cl}$
0.05	100	128	-13.175	-13.371	-16.643
0.05	75	256	-13.786	-14.210	-20.070
0.05	50	512	-13.744	-14.141	-29.402
0.1	100	128	-13.426	-13.463	-16.643
0.1	75	256	-14.198	-14.523	-20.070
0.1	50	512	-14.305	-14.820	-29.402

Table 3.3: Rate constants for DW1 at temperatures 100, 75, 50 K. The number of beads  $N_s$  needed to converge  $k_{\rm red}$  is provided. The QUAPI rate constants  $k_{\rm QUAPI}$  were obtained from Table II in Ref. [65].  $k_{\rm red}$  differs only by a factor of 2 or 3 from  $k_{\rm QUAPI}$ .

temperatures and must be included for an accurate determination of the rate.

## 3.6.2 Multi-state system-bath and reduced dimensional RPIs

The two reduced dimensional RPI formulations for multi-state systems are discussed here: the reduced dimensional MF-RPI (rMFRPI) and the reduced dimensional MV-RPI (rMVRPI). The temperature at which the reduced dimensional multi-state RPIs (rMSRPIs) are determined is 118 K ( $\beta = 2743.43$  a.u.); the dimensionless friction  $\eta/M\omega_0$  is varied over two orders of magnitude, from 0.01 to 1.0.



Figure 3.5: The rMFRPI (left) and rMVRPI (right) are compared with the system MF-RPI for the nonadiabatic model. The dimensionless friction  $\eta/M\omega_0$  is varied as 0.01 (black), 0.1 (red), 0.5 (red), and 1.0 (green) in both plots at T = 118 K. The MF-RPI for the system, i.e., for the case with zero coupling to the bath is show in pink; 256 beads are used to represent the RPs in all cases.

Fig. 3.5 plots the rMFRPI (left subplot) and rMVRPI (right subplot) whose spread decreases with increasing system-bath coupling. This is in keeping with the observations made for adiabatic systems. The two rMSRPI formulations are compared in Fig. 3.6: the rMVRPI is shown to have a larger spread than the rMFRPI.



Figure 3.6: The plot on the left is that of the rMFRPI (continuous black line) and rMVRPI (red dots) determined using 256 RP beads, for nonadiabatic model system, with  $\eta/M\omega_0 = 0.01$  and T = 118 K.

Rate constants  $k_{\text{red,MF}}$  were computed for different values of the dimensionless friction using Eq. 3.53 obtained via the reduced dimensional formulation described in Sec. 3.3.2; Fig. 3.7 compares them to the QUAPI rate constants  $k_{\text{QUAPI}}$ . The two agree with each other to within a factor of 2 to 4; the results are consistent with the expectation that the tunneling rate decays with increase of the systembath coupling. It is to be noted that these are preliminary results, and that the discrepancies between the benchmark QUAPI rates and the reduced system ring polymer rates could be due to the inability of the RP formulation to capture coherence and dynamical recrossing effects, and is under current investigation.



Figure 3.7: Plot of rate constants computed for the symmetric proton tunneling model system as a function of the dimensionless friction parameter  $\eta/M\omega_0$ ;  $k_{\rm red,MF}$  – the rate constant obtained using the reduced dimensional MF-RPI formalism is depicted with black dots and a continuous line; 256 RP beads were used for each case. QUAPI rate constants  $k_{\rm QUAPI}$  are plotted using red dots and a dotted line; they were obtained from the authors of Ref. [64]. The two rates agree with each other within a factor of 2 to 4.

### CHAPTER 4

### TOWARDS THE SIMULATION OF MULTIDIMENSIONAL SYSTEMS

The simulation and modeling of complex molecular systems remains a challenge despite the increase in computational capability. The central problem is the development of efficient methods in the simulation of large scale reactive systems over long time scales. This, therefore, is dependent on advances made in the modeling of potential energy surfaces, in their sampling techniques, and in the accurate description of the dynamics – classical and quantum mechanical.

The oft-used molecular dynamics (MD) models are based on empirical potentials describing the intramolecular and intermolecular interactions; they are unable to describe changes in the electronic structure of the system being studied. 'Ab initio' MD methods compute the potential on the fly, but are computationally demanding [66]. The bottleneck being the computation of the electronic structure at each time step, which restricts the system under investigation to a few hundred atoms, though progress has been made to improve the computational efficiency [67]. QM/MM methods have been used extensively towards the study of biological enzymes successfully; however, the optimal treatment of the boundary between the QM and MM region is an open question [68]. Mixed quantum-classical methods introduce uncontrolled approximations in the feedback forces between the modes described using QM and those described using MD [69]. Recent developments in IVR based methods show that ZPE, tunneling and quantum coherence effects can be captured while ensuring all the modes in the system are treated at the same level of theory [16].

Path integral based methods such as PIMD, RPMD, and its nonadiabatic versions allow for the inclusion of nuclear quantum effects in molecular simulation, while neglecting long time coherence effects [18, 19]. The advantages of path integrals is the ease of extension to multi-dimensional systems; this, coupled with the algorithmic improvements, has led to the development of '*ab initio*' PIMD, which shows immense potential for the simulation of condensed phase systems incorporating nuclear quantum effects [70–72]. The SCI and RPI methods discussed previously have been extended to compute reaction rates and tunneling splittings for complex molecular systems [33,34,37,38,73]. This section presents preliminary results for the extension of the MS-RPI method to multidimensional multi-state systems, and the combination of transition path sampling methods with RPMD to determine ring polymer transition states in quantum systems.

### 4.1 MF-RPIs for systems with conical intersections

Conical intersections (CIs) are ubiquitous in polyatomic molecules and play a significant role in the dynamics of multi-dimensional nonadiabatic systems. The nonadiabatic couplings (NACs), ignored in the Born-Oppenheimer approximation, are responsible for electronic and nuclear coupling. In such systems, the adiabatic description of the electronic and nuclear wavefunctions is insufficient, as the electronic wavefunction changes sign when it traverses around a CI – popularly termed as the geometric phase (GP) effect, or Berry's phase effect – making it double-valued. As the total wavefunction must be a single-valued function, the nuclear wavefunction must also be double-valued in nature. The influence of the GP on the nuclear dynamics suggests that the reaction rates computed in the two representations will differ; it has been demonstrated that the neglect of GP can lead to an overestimation of the rate by two orders of magnitude at low temperatures [74]. Thus, at low temperatures, the nuclear tunneling pathway is influenced by the CI.

The RPI method has been used in the computation of tunneling splittings and

reaction rates for realistic systems [73, 75]. Its extensions to the case of multiple electronic states is an active area of research [45, 76, 77]. This section presents preliminary results obtained in the extension of the MF-RPI formalism – based on the diabatic representation of electronic state as described in Sec. 2.1.1 – to multi-dimensional nonadiabatic systems with conical intersections.

### 4.1.1 Model systems

Two nonadiabatic model systems with conical intersections (CIs) are studied. The plots for the potential energy surfaces are provided in Fig. 4.1 and the corresponding equations for the diabatic potentials and couplings are given below [78].

### 2D Jahn-Teller system

The 2D Jahn-Teller model system consists of two harmonic diabatic potentials with linear coupling along the y mode:

$$V_{11}(x,y) = \frac{M\omega_1^2}{2} \left( x + \frac{a}{2} \right)^2 + \frac{M\omega_2^2}{2} y^2, \qquad (4.1)$$

$$V_{22}(x,y) = \frac{M\omega_1^2}{2} \left(x - \frac{a}{2}\right)^2 + \frac{M\omega_2^2}{2} y^2, \qquad (4.2)$$

$$V_{12}(x,y) = cy, (4.3)$$

where  $a = 6.0, M = 1.0, \omega_1 = \omega_2 = 1.0$ , and c = 1.0.

### Phenol photodissociation

The phenol photodissociation model is used to describe dissociative tunneling of the  $S_1$  state:

$$S_1 \equiv V_{11}(x, y) = \frac{M\omega_1^2}{2} \left( x + \frac{a}{2} \right)^2 + \frac{M\omega_2^2}{2} y^2, \qquad (4.4)$$

$$S_2 \equiv V_{22}(x, y) = Ae^{-\alpha(x+b)} + \frac{M\omega_2^2}{2}y^2,$$
 (4.5)

$$V_{12}(x,y) = cye^{-(x-x_{\rm CI})^2/2\sigma_x^2}e^{-(y-y_{\rm CI})^2/2\sigma_y^2}.$$
 (4.6)

The phenoxyl ring is photoexcited to the  $S_1$  state, which dissociates to produce an H atom and a phenoxyl radical. The dissociation of the low-lying vibrational levels of the first excited state  $(S_1)$  proceeds via nonadiabatic tunneling and is governed by the CI generated by the interaction of the  $S_1$  and  $S_2$  states.



Figure 4.1: Plots of the adiabatic potentials for the Jahn-Teller model system (left); and phenol photodissociation model system (right) obtained by diagonalizing the corresponding diabatic potential energy matrix. All values are in atomic units.

Parameter	a	b	с	α	А	$\omega_1$	$\omega_2$	x <sub>CI</sub>	Усі	$\sigma_x$	$\sigma_y$
Value (a.u.)	4.0	-11.0	2.0	5.0	0.1	1.0	1.0	0.0	0.0	1.274	0.849

Table 4.1: Parameters for the phenol photodissociation system

### 4.1.2 Results and discussion

The diabatic representation implicitly incorporates GP phase effects; the MF-RPIs shown in Fig. 4.2 depict the nonadiabatic tunneling pathway. The MF-RPI capture the expected trends: lowering of the system temperature connects the low-lying vibrational states of the two wells in the JT system, and suggest dissociative tunneling from the low-lying vibrational states in the phenol photodissociation model.



Figure 4.2: Plot of the MF-RPI on the contours of the lower adiabatic potential surface for the Jahn-Teller model system (left) for  $\beta = 5.0, 7.5, 10.0, 20.0$  a.u. are shown as black, green, red, and white points; and the phenol photodissociation model system (right) for  $\beta = 8.0, 9.0, 10.0, 13.0$  a.u. are depicted using black, green, red, and white points, respectively. All values are in atomic units.



Figure 4.3: Plot of the RPI determined at  $\beta = 50.0$  a.u. on the lower adiabat (black) and MF-RPI (red) on the contours of the lower adiabatic eigenstate of the Jahn-Teller model system (left); RPIs determined on the lower adiabat for  $\beta = 25.0, 35.0, 50.0$  a.u. are shown in red, blue and black, respectively (right); the CI at (0,0) is shown as a white dot in both cases. All values are in atomic units.

In Fig. 4.3, a comparison between the RPI determined on the lower adiabatic surface and the MF-RPI is made, by plotting them on the contour of the lower adiabatic eigenstate. The RPI is shown in red and the MF-RPI is in black, while the CI at (0,0) is depicted as a white dot. This illustrates that the single surface RPI does not capture the accurate tunneling pathway, whereas the MF-RPI does so, because it includes the effect of the excited electronic state. The plot on the right in the same figure depicts the RPIs determined on the lower adiabatic eigenstate at  $\beta = 25.0, 30.0, 50.0$  a.u.; this shows that tunneling effects are only seen at much lower temperatures when only the single surface is considered. This is in keeping with the observation that the crossover temperature for nonadiabatic systems, though not clearly defined, must be higher than that of the adiabatic crossover temperature.

### 4.2 Reaction coordinates in quantum systems

Transition state theory and it's quantum mechanical analogues assume a reaction coordinate and transition state – a first order saddle point on the potential energy surface. This allows for the computation of the reaction rate and extraction of mechanistic insight from the dynamics. In complex molecular systems, there are multiple dynamical pathways along which the reaction can occur; this indicates that there are many transition states that lead to the product and the identification of all such transition states is difficult. A popular example is that of protein folding where the collective variables determining the folding pathway depend on both the protein and solvent DoFs.

TPS overcomes these problems by sampling the transition path ensemble (TPE) – a weighted set of reactive trajectories that connect the reactant and product configurations [79,80]. It has the advantage that no assumptions about the reaction coordinate are made. The TPE is an ensemble of reactive trajectories x(t) which begins in the reactant well (R) and ends in the product well (P). It is represented using a sequence of states  $x(t) \equiv \{x_0, x_{\Delta t}, \dots, x_t\}$ , where  $\Delta t = t/N$ . If this is a dynamical trajectory, the variable *x* corresponds to the set of phase space variables *r*, *p*; for a stochastic trajectory, it is just the configuration of the system. The contribution of a given path to the TPE is determined by its statistical weight  $\mathcal{P}_{RP}[x(t)]$  which is dependent on the initial conditions and the propagation rules for the time evolution. For a stochastic trajectory x(t), it is a product of the short time transition probabilities and the initial distribution of states  $\rho(x)$  [79,81]:

$$\mathcal{P}_{RP}[x(t)] \equiv h_R(x_0) \frac{\left[\rho(x_0) \prod_{i=0}^{N-1} p(x_{i\Delta t} \to x_{(i+1)\Delta t})\right]}{\mathcal{Z}_{RP}(t)} h_P(x_t).$$
(4.7)

Here,  $h_R(x_0)$  and  $h_P(x_t)$  are the population functions for the reactant and product wells. They are equal to one if the time point  $x_0$  and  $x_t$  are in the defined reactant and product states, and zero otherwise. This restricts the paths considered to those that are reactive.  $Z_{RP}(t)$  is the normalization factor for the distribution:

$$\mathcal{Z}_{RP}(t) = \int \mathcal{D}[x(t)] h_R(x_0) \left[ \rho(x_0) \prod_{i=0}^{N-1} p(x_{i\Delta t} \to x_{(i+1)\Delta t}] h_P(x_t), \quad (4.8)$$

and is obtained by summing over all paths that make up TPE – a subset of reactive trajectories *selected* from the set of all trajectories produced by the dynamics.

The sampling of the TPE is an importance sampling of reactive trajectories and is accomplished as follows: starting with a reactive trajectory  $x^{\text{old}}(t)$  with weight  $\mathcal{P}_{RP}[x^o(t)]$ , a new trajectory  $x^{\text{new}}(t)$  is generated and accepted with a probability. The detailed balance criterion must be satisfied:

$$\mathcal{P}_{RP}[x^{\text{old}}(t)]\pi[x^{\text{old}}(t) \to x^{\text{new}}(t)] = \mathcal{P}_{RP}[x^{\text{new}}(t)]\pi[x^{\text{new}}(t) \to x^{\text{old}}(t)], \qquad (4.9)$$

where  $\pi[x^{\text{old}}(t) \to x^{\text{new}}(t)]$  is the conditional probability of moving to the new trajectory  $x^{\text{new}}(t)$  from the old trajectory  $x^{\text{old}}(t)$ . This has two contributions: The probability of generation of the new trajectory  $\mathcal{P}_{\text{gen}}[x^{\text{old}}(t) \to x^{\text{new}}(t)]$  and the probability of its acceptance  $\mathcal{P}_{\text{acc}}[x^{\text{old}}(t) \to x^{\text{new}}(t)]$ . Using the Metropolis algorithm, the
acceptance probability is defined as:

$$\mathcal{P}_{\rm acc}[x^{\rm old}(t) \to x^{\rm new}(t)] = h_R(x_0^{\rm new})h_P(x_t^{\rm new})\min\left\{1, \frac{\mathcal{P}_{RP}[x^{\rm new}(t)]}{\mathcal{P}_{RP}[x^{\rm old}(t)]}\frac{\mathcal{P}_{\rm gen}[x^{\rm new}(t) \to x^{\rm old}(t)]}{\mathcal{P}_{\rm gen}[x^{\rm old}(t) \to x^{\rm new}(t)]}\right\}$$

$$(4.10)$$

Shooting moves and shifting moves can be employed to generate new trajectories  $x^{\text{new}}(t)$  [81].

The statistical analysis of the transition paths can be used to identify reaction coordinates and transition states. In complex systems, the transition states (TSs) are defined as configurations that can relax to either the reactant well or the product well with equal probability. The set of all such TSs is the *separatrix* which separates the stable reactant and product wells from each other. The committor function:

$$p_P(x,t_s) \equiv \frac{\int \mathcal{D}[x(t)]\mathcal{P}[x(t_s)]\delta(x_0 - x)h_P(x_{t_s})}{\int \mathcal{D}[x(t)]\mathcal{P}[x(t_s)]\delta(x_0 - x)},$$
(4.11)

is used to determine the probability that the system configuration x will reside in the product well at time  $t_s$ . Here,  $\mathcal{P}[x(t_s)]$  is the statistical weight of the trajectory  $x(t_s)$  in the ensemble of trajectories initialized at x and propagated for time  $t_s$ . The  $h_P(x_{t_s})$  in the numerator selects trajectories that reach the the product well at time  $t_s$ . An analogous committor function can be defined for the reactant well,  $p_R(x, t_s)$ ; if these committor functions are equal for for a configuration x, then is a part of the *separatrix*.

This chapter demonstrates that the TPS method can be extended reliably to the study of quantum mechanical systems, and to determine TSs. Some preliminary results for 1D systems are presented here, extensions to multi-dimensional systems will require algorithmic improvements.

### 4.2.1 Model systems and simulation details

The 1D Eckart barrier is used to demonstrate the use of TPS whose potential is given as:

$$V(x) = b \operatorname{sech}^2 \frac{x}{a} \tag{4.12}$$

with parameters,  $b = 13.5/\pi$  and a = 0.66 [59]. The inverse temperature  $\beta = 3.5$ a.u. and 16 RP beads were used to model the quantum particle with mass M = 1a.u. The reactant and product configurations were defined as configurations with the centroid  $\bar{x} = \sum_{\alpha=1}^{N} x_{\alpha}$  to the left of x = -4 a.u., and to the right of x = 4.0 a.u., respectively. RPMD trajectories [18] were propagated for a total of 550 time steps using the velocity verlet algorithm with each time step  $\Delta t = 0.01$  a.u. Hamilton's equations for the system were obtained from Eq. 1.18:

$$\dot{x}_{\alpha} = \frac{\partial H_{\rm RP}}{\partial p_{\alpha}} = \frac{p_{\alpha}}{M} \tag{4.13}$$

$$\dot{p}_{\alpha} = -\frac{\partial H_{\rm RP}}{\partial x_{\alpha}} = -\frac{M}{\beta_N^2} (2x_{\alpha} - x_{\alpha-1} - x_{\alpha+1}) - V'(x_{\alpha}) \tag{4.14}$$

The TPE was sampled by performing shooting and shifting moves of the RP centroid.

# 4.2.2 Results and discussion

The committors for 1D symmetric Eckart barrier were determined and the statistical analysis yielded an ensemble of ring polymer transition states, as shown in Fig. 4.4. It is seen that the committor probability for a RP configuration initialized at values closer to the reactant region has a low probability of reaching the products, but for those initialized near the barrier, it attains values around 0.5 indicating that we are near the separatrix. Its value is close to or equal to 1 for points initialized to the right of the barrier reflecting that the probability of reaching the product state is higher, which is in keeping with physical intuition. A representative TS is also shown in Fig. 4.4 which drapes over the barrier and has an extended configuration of the RP beads.



Figure 4.4: Representative plots for the committor (left) and ring polymer transition states (right) for the 1D Eckart barrier.

#### CHAPTER 5

# ELECTRICAL CONDUCTIVITY IN METAL-ORGANIC FRAMEWORKS

The field of metal-organic frameworks (MOFs) has seen intense activity since its inception in the last decade of the 20th century. It utilizes the vast knowledge of organic and inorganic chemistry developed during the last two hundred years. The multiple oxidation states of transition metal (TM) ions and the ease of synthesis of diverse organic linkers, and the possibility of post-synthetic modification allows for the facile tuning of chemical and physical properties of the synthesized materials with applications in gas storage, separation, drug delivery, molecular magnetism, and catalysis [82]. The electrical conductivity of porous MOFs is, typically, low, due to the use or redox-inactive organic ligands that bind to the metal ions, but there has been a recent surge in interest towards the design of MOFs that exhibit porosity and high charge mobility and electrical conductivity [83]. Specifically, the incorporation of mixed-valency in MOFs by a judicious choice of redox-noninnocent metal ions and ligands, shows promise towards the development of highly conductive MOFs [84].

Intervalence charge transfer (IVCT) is the delocalization of charge due to electronic coupling between two or more moieties in a mixed-valence compound [85]. The Robin Day scheme categorizes mixed-valence compounds into three classes, based on the extent of charge delocalization between two sites: (1) class I – electrons localized at the two sites; (2) class II – thermally/optically accessible IVCT; (3) class III – electrons are delocalized between the two sites. MOFs can be perceived as a collection of such molecular moieties and this classification can be used to predict charge transport mechanisms: In MOFs with extensive charge delocalization (class III compounds), the charge transport will be band-like; whereas, for systems similar to class II compounds, charge hopping is the predominant transport mechanism.

The dominant mechanism governing the electrical conductivity can be determined by examining its temperature dependence. Hopping transport is prevalent in materials with localized charge carriers which are transferred from one site to the other when external (thermal) energy is provided; thus, the electrical conductivity increases with increasing temperature:

$$\sigma = \sigma_0 e^{-(T_0/T)^{1/d}},\tag{5.1}$$

where  $\sigma$  is the electrical conductivity at temperature T;  $T_0$ ,  $\sigma_0$  are constants specific to the sample, and d is its dimensionality. Band transport, however, can be either thermally activated or deactivated. For metallic systems, the back scattering of the conduction band electrons from the lattice sites becomes significant at higher temperatures reducing the conductivity; for semiconductors, however, electrons are promoted to the conduction band as the temperature increases resulting in an increase of the electrical conductivity. This chapter describes the preliminary results of the theoretical approaches taken to explain the observed conductivities.

# 5.1 The electronic structure of 2D metal-semiquinoid MOFs

Recent studies have focused on a systematic study of the electronic structure of these materials, in the hope that general design principles can be formulated for the synthesis of highly conductive MOFs [86, 87]. 2D metal-semiquinoid MOFs show immense promise as energy storage materials due to their exceptionally high electrochemical capacities. These frameworks incorporate the 2,5dihydroxybenzoquinone (H<sub>2</sub>dhbq) and its analogues as the organic linkers, as shown in Fig. 5.1. These linkers can exist in three different redox states in molecular complexes and extended solids as shown in Fig. 5.2 – there are no unpaired electrons on dhbq<sup>2–</sup> and thb<sup>4–</sup> (1,2,4,5-tetrahydroxybenzene), whereas dhbq<sup>3–</sup> has one unpaired electron. They mediate the electronic coupling between the TM ions



Figure 5.1: A cartoon representation of the building unit of the 2D and 3D material with metal atom flanked by two dhbq<sup>3–</sup> linkers and one dhbq<sup>2–</sup> linker.

allowing for electron transport and long range magnetic ordering. Experimentally,



Figure 5.2: The possible redox states of the ligand  $H_2$ dhbq upon deprotonation. The frequencies of the carbonyl stretches are also provided in cm<sup>-1</sup>.

both 2D and 3D materials were synthesized by combining these ligands with first row transition metals: Ti, V, Cr, and Fe. The general formula for these materials is given by  $(\text{cation})_2M_2(X_2\text{dhbq})_3$ , where X can be a proton or a halide; the cation for the Fe system is NBu<sub>4</sub><sup>+</sup> (tetra-n-butyl ammonium) and for the Ti, V and Cr systems, it is H<sub>2</sub>NMe<sub>2</sub><sup>+</sup> (dimethyl ammonium). The frequency of the carbonyl stretching mode  $\nu_{C=O}$  determined using infrared spectroscopy is an indicator of the redox state of the ligands in these materials. As the ligands are reduced by postsynthetic modification, the vibrational frequency of the carbonyl bond reduces; for instance, in the Cr system, the two features are observed: one at 1540cm<sup>-1</sup> corresponding to the dianion, dhbq<sup>2-</sup>, and another at 1450cm<sup>-1</sup> corresponding to the trianion, dhbq<sup>3-</sup>. The broad absorption in the V system is indicative of a delocalized system and the material is classified as belonging to class III in the Robin-Day scheme. The infrared spectra is inconclusive for the Fe system, and the results of UV-Vis-NIR reflectance spectroscopy were provided as evidence to classify it as belonging to the Robin-Day Class II/III mixed-valency [88].



Figure 5.3: Infrared spectra for the Ti, V, and Cr materials (left); this figure is reprinted with permission from *J. Am. Chem. Soc.* 2018, 140, 8, 3040–3051. Copyright (2018) American Chemical Society. Spectra for the Fe MOF (right) are reprinted with permission from *J. Am. Chem. Soc.* 2015, 137, 50, 15703–15711. Copyright (2015) American Chemical Society.

Results of the variable-temperature two-point electronic conductivity measurements for the materials considered are presented in Fig. 5.4 and their conductivities at 298 K are tabulated in Table. 5.1. It is seen that the conductivity increases with increasing temperature. It is suspected that the mixed-valence states in Cr and Ti



Figure 5.4: Variable temperature conductivity measurements for the Ti, V, and Cr materials (left); this figure is reprinted with permission from *J. Am. Chem. Soc.* 2018, 140, 8, 3040–3051. Copyright (2018) American Chemical Society. Results for the Fe MOF (right) are reprinted with permission from *J. Am. Chem. Soc.* 2015, 137, 50, 15703–15711. Copyright (2015) American Chemical Society.

ТМ	$\sigma~({ m S~cm^{-1}})$
Ti	$2.7 \times 10^{-3}$
V	0.45
$\operatorname{Cr}$	$1.2 \times 10^{-4}$
Fe	0.16

Table 5.1: Electrical conductivity ( $\sigma$ ) for the different TM materials. Data for Ti, V, and Cr based MOFs was obtained from Ref. [86] and for the Fe based MOF was obtained from Ref. [88]

are localized, whereas that of Fe and V are delocalized [86,88].

## 5.2 Simulation details

The Cr and Fe based MOFs are discussed in this section. The first step in the study of the MOFs is the selection of the appropriate molecular fragment from the extended structure that can capture all the relevant electronic properties [89]. Six metal center complexes were chosen as a representative molecular fragment; they are depicted in Fig. 5.5. These fragments were obtained from the geometry optimizations of the extended MOF. The optimization was carried out with the VASP electronic structure package using the PBE exchange-correlation functional; both atomic positions and lattice parameters were allowed to relax [90].



Figure 5.5: The six-center molecular fragment for the Fe system obtained from the extended MOF. The ligand has Cl atoms (green) instead of hydrogens at the 2 and 5 positions and the ends of the uncoordinated hydroxyl groups were capped using protons.

The uncoordinated hydroxyl groups are protonated to ensure that the net charge on the molecular fragments is zero. Single point energy calculations were performed using the DFT hybrid functionals  $\omega$ B97 and M11; the 6-31G(df,p) basis was used for all the atoms. The charges of these molecular fragments are chosen to be 0, -2, -4, and -6; this allows for the study of the localization of charge in these systems and the determination of single point energies determined. Restricting the total number of electrons to an even number ensures the spin multiplicity of fragment is 1. Furthermore, atomic charges was determined using the CHELPG scheme.

n	$C_{\omega B97,n}$	$\Delta_{\omega \mathrm{B97,n}}$	$\mathrm{C}_{\mathrm{M11,n}}$	$\Delta_{M11,n}$
0	7.70	0	8.18	0
-2	7.76	0.06	8.23	0.05
-4	7.68	-0.02	8.52	0.34
-6	8.03	0.33	8.48	0.3

Table 5.2: The sum of the atomic charges  $(C_{\omega B97,n})$  at the six Cr centers computed for the fragments with total charge n = 0, -2, -4 and -6.  $\Delta_{\omega B97,n}$  and  $\Delta_{M11,n}$ represent the change with respect to the n = 0 fragment.

### 5.3 Results and discussion

The sum of the atomic charges at the metal centers in fragments with zero net charge ( $C_{\omega B97,0}$ ) and in fragments with a net negative charge is tabulated in Tables 5.2 and 5.3. The change in the total atomic charges at the six metal centers,  $\Delta_{\omega B97,n} = C_{\omega B97,n} - C_{\omega B97,0}$ , upon addition of electrons to the fragment in steps of two is determined. This is a measure of the electrons accepted by the metal centers and the qualitative trend is found to be the same for both the  $\omega B97$  and M11 hybrid functionals. For the Cr system, the change in the atomic charges is a negligible fraction of the electrons added to the fragment; the excess electrons primarily reduce the ligands. However, in the Fe molecular fragment, both the Fe centers and the ligands are reduced.

n	$C_{\omega B97,n}$	$\Delta_{\omega \mathrm{B97,n}}$	$\mathrm{C}_{\mathrm{M11,n}}$	$\Delta_{M11,n}$
0	7.62	0	7.88	0
-2	7.12	-0.50	7.65	-0.23
-4	6.40	-1.22	6.93	-0.95
-6	5.85	-1.77	6.23	-1.55

Table 5.3: The sum of the atomic charges  $(C_{\omega B97,n})$  at the six Fe centers computed for the fragments with total charge n = 0, -2, -4 and -6.  $\Delta_{\omega B97,n}$  and  $\Delta_{M11,n}$ represent the change with respect to the n = 0 fragment.

These results suggest that the probable mechanism of electron transport in the

Cr and Fe systems is *via* thermally activated hopping. The computation of the relative electrical conductivities of these systems is a work in progress.

#### CHAPTER 6

#### CONCLUSIONS AND FUTURE DIRECTIONS

The dissertation is primarily focused on the study of charge transport in nonadiabatic systems using the path integral formalism. It relies on the equivalence of the statistical properties of a classical ring polymer and that of a quantum particle. The multi-state ring polymer instanton was introduced in Chapter 2 and shown to compute nonadiabatic rates accurately in the coherent tunneling regime. The method accurately predicts the electron transfer rates for over three orders of magnitude of electronic coupling, ranging from the weak to strong coupling between the donor and acceptor states. Chapter 3 extends the RPI formulation to the condensed phase via system-bath and reduced dimensional RP formulations. The two formalisms were developed for both adiabatic and multi-state condensed phase systems; it was demonstrated that the sbRPIs and rRPIs agreed with each other. The incoherent tunneling rate was determined using the reduced dimensional formulation of the RP and the "Im F" approximation to it and the results obtained agreed with the benchmark QUAPI rate constants, to within a factor of order unity. Chapter 4 presents preliminary results towards the study of multidimensional multi-state systems. In particular, nonadiabatic systems with conical intersections were studied; the MF-RPI captures the accurate tunneling pathway as opposed to the SS-RPI which excludes the excited state. Also, preliminary results combining transition path sampling methods with RPMD were explored. Chapter 5 describes the electronic structure of Fe and Cr based metalorganic frameworks. It explores the localization properties of electrons added to a representative six-center molecular fragment of the MOF; the prediction of the conductivity trends is a work in progress.

In the context of the multi-state RPI methods discussed in this thesis, two beads

are constrained to the crossing of the diabatic states. Algorithmic improvements that obviate this constraint, and that which would allow for the determination of the instanton without performing multiple calculations would prove extremely useful in extending the method to the study of realistic molecular systems. Another avenue that is of considerable interest is the development of a multi-state microcanonical instanton rate theory that works in both the adiabatic and nonadiabatic limits. The combination of TPS with RPMD and MF-RPMD will be particularly useful in the identification of reaction coordinates of adiabatic and multi-state quantum systems. The centroid coordinate alone was used to compute the committor here; next steps to study the Eckart barrier would be include the low frequency normal modes of the RP in the analysis to determine more accurate committors and RP TSs.

#### APPENDIX A

# ZERO MODE OF THE MEAN-FIELD RING POLYMER INSTANTONS

The MF action from the continuous  $(N \to \infty)$  limit of the effective MF ring polymer potential

$$S_{\rm MF} = \lim_{N \to \infty} \beta_N V_{\rm MF}$$

$$= \lim_{N \to \infty} \beta_N \left[ \frac{M}{2\beta_N^2} \sum_{\alpha} (\mathbf{R}_{\alpha} - \mathbf{R}_{\alpha+1})^2 - \frac{1}{\beta_N} \ln \Gamma_{\rm MF} \right]$$

$$= \int_0^\beta d\tau \left[ \frac{M}{2} \left( \frac{d\mathbf{R}(\tau)}{d\tau} \right)^2 - \frac{d\ln|\Gamma_{\rm MF}[\mathbf{R}(\tau)]|}{d\tau} \right]$$

$$= \int_0^\beta d\tau \left[ \frac{M}{2} \left( \frac{d\mathbf{R}(\tau)}{d\tau} \right)^2 + \mathcal{V}_{\rm MF} \right] \qquad (A.1)$$

Here,  $-\frac{d \ln |\Gamma_{\rm MF}[\mathbf{R}(\tau)]|}{d\tau}$  is defined as  $\mathcal{V}_{\rm MF}$  for clarity of presentation. Note that in obtaining Eq. A.1, the finite difference definition of a derivative for the nuclear term is used, and the integral of a differential operator in  $\tau$  for the  $\ln |\Gamma_{\rm MF}|$  term is introduced. Setting the first variation of the action to zero, Newton's equations in imaginary time on the inverted potential is obtained,

$$\delta S_{\rm MF} = -M \frac{d^2 \mathbf{R}(\tau)}{d\tau^2} + \nabla_{\mathbf{R}} \mathcal{V}_{\rm MF} = 0. \tag{A.2}$$

The MF instanton is the solution to these  $N \times f$  equations.

The instanton is an unstable periodic orbit, and this is established by calculating the eigenvalues of the stability matrix. The stability matrix from the second variation of the action  $\delta^2 S_{\rm MF}$  is,

$$\Lambda_{\rm MF} \equiv -M \frac{d^2}{d\tau^2} + \nabla_{\mathbf{R}} \nabla_{\mathbf{R}}^T \mathcal{V}_{\rm MF}.$$
 (A.3)

Differentiating Eq. A.2 with respect to imaginary time, it is easy to see

$$\frac{d}{d\tau} \left[ -M \frac{d^2 \mathbf{R}(\tau)}{d\tau^2} + \nabla_{\mathbf{R}} \mathcal{V}_{\mathrm{MF}} \right] = 0$$
$$\left[ -M \frac{d^2}{d\tau^2} + \nabla_{\mathbf{R}} \nabla_{\mathbf{R}}^T \mathcal{V}_{\mathrm{MF}} \right] \dot{\mathbf{R}}(\tau) = 0 \times \dot{\mathbf{R}}(\tau).$$
(A.4)

It is clear that Eq. A.4 is the eigenvalue equation corresponding to operator  $\Lambda_{MF}$  and the zero-mode is the velocity mode,  $\dot{\mathbf{R}}(\tau)$ , with a zero eigenvalue. This analysis can be extended in a straightforward manner to MV-RPI and the reduced dimensional single surface and multi-state RPIs.

# APPENDIX B

# ATOMIC COORDINATES FOR THE FE AND CR MOLECULAR FRAGMENTS

The coordinates for the symmetry unique atoms alone are provided below for the Fe and Cr systems. Both the fragments considered here contain a  $C_3$  axis of symmetry passing through the center of the ring, perpendicular to it.

С	6.0	-6.13047	0.60269	1.26231
$\mathbf{C}$	6.0	1.81696	11.75210	1.26107
$\mathbf{C}$	6.0	-0.41036	-11.88191	1.25621
$\mathbf{C}$	6.0	7.53708	-0.73251	1.25497
$\mathbf{C}$	6.0	-7.52801	0.73144	-1.26028
$\mathbf{C}$	6.0	0.41942	11.88084	-1.26152
$\mathbf{C}$	6.0	-1.81138	-11.75303	-1.26415
$\mathbf{C}$	6.0	6.13606	-0.60363	-1.26539
$\mathbf{C}$	6.0	-11.76632	-5.72081	-0.61814
$\mathbf{C}$	6.0	-3.81889	5.42859	-0.61938
$\mathbf{C}$	6.0	1.89738	-7.05611	-0.62229
$\mathbf{C}$	6.0	9.84481	4.09328	-0.62353
$\mathbf{C}$	6.0	-9.84825	-4.08732	0.61689
$\mathbf{C}$	6.0	-1.90082	7.06209	0.61565
$\mathbf{C}$	6.0	3.81590	-5.42152	0.61272
$\mathbf{C}$	6.0	11.76333	5.72789	0.61148
$\mathbf{C}$	6.0	-8.91323	5.90960	0.61643
$\mathbf{C}$	6.0	10.46641	-7.90470	0.60796
$\mathbf{C}$	6.0	-3.19620	-6.56877	0.61205
$\mathbf{C}$	6.0	4.75123	4.58063	0.61081
С	6.0	-4.75246	-4.58104	-0.61440
$\mathbf{C}$	6.0	3.19498	6.56837	-0.61564
С	6.0	-10.47113	7.89522	-0.61075
С	6.0	8.90851	-5.91907	-0.61922

Table B.1: Coordinates of symmetry unique Carbon atoms for the Fe molecular fragment

17.0	-8.34911	0.80788	-2.72105
17.0	-0.40167	11.95728	-2.72229
17.0	-2.63417	-11.67696	-2.72427
17.0	5.31327	-0.52755	-2.72551
17.0	-5.31086	0.52494	2.72353
17.0	2.63658	11.67434	2.72229
17.0	0.40575	-11.96054	2.71957
17.0	8.35318	-0.81115	2.71833
26.0	7.20756	3.37574	-0.00064
26.0	6.45511	-4.71057	-0.00594
8.0	-12.72180	-6.43535	-1.05588
8.0	-4.77437	4.71405	-1.05712
8.0	0.94100	-7.76886	-1.05985
8.0	8.88844	3.38053	-1.06109
8.0	-8.89129	-3.37642	1.05678
8.0	-0.94385	7.77298	1.05554
8.0	4.77248	-4.70909	1.05108
8.0	12.71992	6.44032	1.04984
8.0	-8.11223	5.02544	1.05370
8.0	11.26740	-8.78885	1.04523
8.0	-2.39766	-7.45609	1.04838
8.0	5.54977	3.69331	1.04714
8.0	-5.55034	-3.69288	-1.04970
8.0	2.39709	7.45652	-1.05094
8.0	-11.26849	8.78376	-1.04656
8.0	8.11115	-5.03054	-1.05503
1.0	-11.51350	9.48590	-0.23602
1.0	10.95665	-9.09843	2.05398
	$\begin{array}{c} 17.0\\ 17.0\\ 17.0\\ 17.0\\ 17.0\\ 17.0\\ 17.0\\ 17.0\\ 26.0\\ 26.0\\ 8.0\\ 8.0\\ 8.0\\ 8.0\\ 8.0\\ 8.0\\ 8.0\\ 8$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	17.0 $-8.34911$ $0.80788$ $17.0$ $-0.40167$ $11.95728$ $17.0$ $-2.63417$ $-11.67696$ $17.0$ $5.31327$ $-0.52755$ $17.0$ $-5.31086$ $0.52494$ $17.0$ $2.63658$ $11.67434$ $17.0$ $2.63658$ $11.67434$ $17.0$ $0.40575$ $-11.96054$ $17.0$ $8.35318$ $-0.81115$ $26.0$ $7.20756$ $3.37574$ $26.0$ $6.45511$ $-4.71057$ $8.0$ $-12.72180$ $-6.43535$ $8.0$ $-4.77437$ $4.71405$ $8.0$ $0.94100$ $-7.76886$ $8.0$ $8.8844$ $3.38053$ $8.0$ $-8.89129$ $-3.37642$ $8.0$ $-0.94385$ $7.77298$ $8.0$ $4.77248$ $-4.70909$ $8.0$ $12.71992$ $6.44032$ $8.0$ $-2.39766$ $-7.45609$ $8.0$ $5.54977$ $3.69331$ $8.0$ $2.39709$ $7.45652$ $8.0$ $2.39709$ $7.45652$ $8.0$ $8.11115$ $-5.03054$ $1.0$ $-11.51350$ $9.48590$ $1.0$ $10.95665$ $-9.09843$

Table B.2: Coordinates of symmetry unique Chrloein, Iron, Oxygen and Hydrogen atoms for the Fe molecular fragment

С	6.0	-0.45504	5.97816	1.16144
С	6.0	11.84556	0.07222	1.16144
С	6.0	-11.72002	-1.72150	1.16144
С	6.0	0.58057	-7.62743	1.16144
С	6.0	-0.58057	7.62744	-1.15975
С	6.0	11.72002	1.72150	-1.15975
С	6.0	-11.84556	-0.07222	-1.15975
С	6.0	0.45504	-5.97815	-1.15975
С	6.0	-7.70662	10.52935	-0.59750
С	6.0	4.59397	4.62341	-0.59750
С	6.0	-6.67102	-3.07624	-0.59750
С	6.0	5.62957	-8.98218	-0.59750
С	6.0	-5.62957	8.98218	0.59919
С	6.0	6.67101	3.07624	0.59919
С	6.0	-4.59397	-4.62341	0.59919
С	6.0	7.70662	-10.52934	0.59919
С	6.0	4.20521	9.73076	0.59919
С	6.0	-7.05977	2.03111	0.59919
С	6.0	5.24082	-3.87483	0.59919
С	6.0	-6.02417	-11.57448	0.59919
С	6.0	6.02416	11.57448	-0.59750
$\mathbf{C}$	6.0	-5.24083	3.87483	-0.59750
$\mathbf{C}$	6.0	7.05977	-2.03111	-0.59750
$\mathbf{C}$	6.0	-4.20522	-9.73076	-0.59750

Table B.3: Coordinates of symmetry unique Carbon atoms for the Cr molecular fragment

$\operatorname{Cr}$	24.0	4.44540	-6.50385	0.00084
$\operatorname{Cr}$	24.0	-3.40979	-7.10175	0.00084
Ο	8.0	-8.64485	11.31462	-1.08834
Ο	8.0	3.65574	5.40868	-1.08834
Ο	8.0	-7.60925	-2.29098	-1.08834
Ο	8.0	4.69134	-8.19691	-1.08834
Ο	8.0	-4.69134	8.19691	1.09003
Ο	8.0	7.60925	2.29098	1.09003
Ο	8.0	-3.65574	-5.40868	1.09003
Ο	8.0	8.64485	-11.31461	1.09003
Ο	8.0	3.39664	8.81254	1.09003
Ο	8.0	-7.86834	1.11289	1.09003
Ο	8.0	4.43225	-4.79305	1.09003
Ο	8.0	-6.83273	-12.49270	1.09003
Ο	8.0	6.83273	12.49271	-1.08834
Ο	8.0	-4.43226	4.79305	-1.08834
Ο	8.0	7.86834	-1.11288	-1.08834
Ο	8.0	-3.39665	-8.81254	-1.08834
Η	1.0	-0.62872	8.26005	-2.04855
Η	1.0	11.67187	2.35411	-2.04855
Η	1.0	-11.89371	0.56039	-2.04855
Η	1.0	0.40688	-5.34555	-2.04855
Η	1.0	-0.40688	5.34555	2.05024
Η	1.0	11.89371	-0.56038	2.05024
Η	1.0	-11.67187	-2.35411	2.05024
Η	1.0	0.62872	-8.26004	2.05024
Η	1.0	7.21638	13.11902	-0.26947
Η	1.0	-9.05928	11.93855	-0.28275

Table B.4: Coordinates of symmetry unique Cr, Oxygen, and Hydrogen atoms for the Cr molecular fragment

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