

Cyber Training Workshop 2023

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Introduction:

In the Kretchmer group at the Georgia Institute of Technology, we're interested in developing new methods for describing electron dynamics. One method we've been working on is called Kinetically Constrained Ring Polymer Molecular Dynamics (KC-RPMD) developed to describe electronic transfer dynamics in condensed phase systems. Though KC-RPMD has been shown to accurately predict ET rate constants in condensed phase systems exhibiting both non-adiabatic and adiabatic dynamics, KC-RPMD has not yet been applied to systems which exhibit ET transfer contributions from both adiabatic and non-adiabatic regimes. With the eventual goal of applying KC-RPMD to describe ET dynamics at electrode interfaces, we've devised a model system that can be used to test KC-RPMD for its ability to simultaneously describe both adiabatic and non-adiabatic dynamics based on the spin-boson model with donor-acceptor dependent electronic coupling which moves along a double-well potential. The model system is based on the anticipated environment seen at electrode interfaces which we plan to apply KC-RPMD to in collaboration with the McDaniel group at Georgia Tech. To test the integrity of KC-RPMD in describing electrode interface systems, we've developed the need to benchmark against an accurate method. The focus of this mini project is to apply the well-established Hierarchical Equations of Motion (HEOM) to solve for exact ET rate constants and eventually reproduce the results from Shi's 2009 publication. Once we reproduce the publication results, we plan to use HEOM to solve for this spin-boson electrode double layer model system in preparation to benchmark against KC-RPMD.

- ET Rate Constants

Electron transfer rate constants assume that dynamics is primarily dominated by first-order kinetics and that the time dependence of the state populations can be described by the kinetic equations (for a 2-level system):

$$\dot{P}_0(t) = -k_f P_0(t) + k_b P_1(t)$$

$$\dot{P}_1(t) = k_f P_0(t) - k_b P_1(t)$$

Where population is conserved $P_0(t) + P_1(t) = 1$ and where k_f and k_b are the forward and backward ET rate constants respectively which are assumed to remain constant within the time it takes to reach steady state equilibrium. The solution to the kinetic equations at equilibrium lead to the detailed balance relationship:

$$\lim_{t \rightarrow \infty} \dot{P}_0(t) = -k_f \langle P_0 \rangle + k_b \langle P_1 \rangle = 0$$

Which gives the relationship between k_f and k_b with respect to the equilibrated electronic populations $\langle P_0 \rangle$ and $\langle P_1 \rangle$. The phenomenological kinetic equations when solved for just $P_0(t)$:

$$P_0(t) = \langle P_0 \rangle + (P_0(0) - \langle P_0 \rangle) e^{-tk_f/(1-\langle P_0 \rangle)}$$

Finally, the ET rate constant assumes the electronic population entirely on the reactant basin with the surrounding nuclei in thermodynamic equilibrium. This will be relevant later for determining rate constants from HEOM.

In addition to solutions from HEOM, for systems following the assumptions of Marcus theory, in the weak coupling regime the ET rate predicted from Marcus theory follows the non-adiabatic rate expression:

$$k_{ET}^{nad} = \frac{2\pi}{\hbar} |K|^2 \sqrt{\frac{\beta}{4\pi\lambda}} \exp \left[-\beta \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \right]$$

- HEOM overview:

HEOM is a numerically exact technique which solves for the reduced density matrix " $\hat{\rho}$ " of open quantum systems coupled to a set of harmonic bath modes. The total Hamiltonian of an open system "S" coupled to a reservoir "R" takes on the general form:

$$H = H_S + H_{SR} + H_R$$

The reduced density matrix " $\hat{\rho}$ " which averages the full density matrix over the reservoir degrees of freedom evolves in time as described by the general equation of motion:

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} [H_S, \hat{\rho}(t)] - \frac{i}{\hbar} \text{tr}\{[H_{SR}, \hat{W}(t)]\}$$

The equation of motion resembles the Louisville-von Neumann equation but with an additional dissipative term describing the system reservoir interaction. This additional dissipative term tends to be the most challenging to deal with, as such, HEOM is one of the few techniques capable of numerically exact solutions to this type of problem.

In the original HEOM formalism, the system Hamiltonian " H_S " spans a single electronic degree of freedom which can be expressed in terms of discrete electronic states $\{|n\rangle\}$, while the reservoir Hamiltonian " H_R " spans a set of uncoupled nuclear harmonic bath coordinates which are further assumed to be linearly coupled to the electronic degrees of freedom through the system-reservoir Hamiltonian " H_{SR} ". The total system Hamiltonian as implemented in the Libra package takes on the form (in atomic units $\hbar = 1$ and mass reduced coordinates):

$$H = \sum_{n,m=0}^{N-1} (|n\rangle H_{nm} \langle m|) + \sum_{n=0}^{N-1} \left(|n\rangle \sum_{b=0}^{N-1} \left(\frac{p_{b,n}^2}{2} + \frac{1}{2} \omega_{b,n}^2 x_{b,n}^2 + f_{b,n} x_{b,n} \right) \langle n| \right)$$

Where the electronic states are indexed by “n” and the reservoir bath coordinates are indexed by nuclear degree of freedom “b”. The set of coefficients “ $f_{b,n}$ ” describe the system bath interaction, which along with the distribution of bath mode frequencies “ $\omega_{b,n}$ ” is fully defined by system bath spectral density distribution:

$$J_n(\omega) = \frac{\pi}{2} \sum_{b=0}^{N_n-1} \frac{f_{b,n}^2}{\omega_{b,n}} \delta(\omega - \omega_{b,n})$$

HEOM is typically implemented with the assumption that the system bath interaction is described by a Debye spectral density which takes on the form:

$$J_n(\omega) = \frac{\eta\gamma\omega^2}{\omega^2 + \gamma^2}$$

Where “ η ” relates to the system-bath coupling strength and “ γ ” is the cutoff frequency relating to the time scale of system-bath dynamics. Additionally, the autocorrelation function of a bath described by the Debye spectral density takes on the form:

$$C(t > 0) = \sum_{k=0}^{\infty} c_k \exp(-\gamma_k t)$$

Where $\gamma_0 = \gamma$ and the summation coefficients:

$$c_0 = \frac{\hbar\eta\gamma^2}{2} \left[\cot\left(\frac{\beta\hbar\gamma}{2}\right) - i \right]$$

$$c_{k>0} = \frac{2\eta\gamma^2}{\beta} \frac{\gamma_k}{\gamma_k^2 - \gamma^2}$$

This also gives rise to the Matsubara frequencies $\gamma_{k>0}$, which may or may not contribute significantly to the overall autocorrelation function depending on the temperature and the strength of the system-bath interaction. The Matsubara frequencies for the Debye spectral density are:

$$\gamma_{k>0} = \frac{2\pi k}{\beta\hbar}$$

The HEOM formalism involves an infinite series of auxiliary density matrices “ ρ_n ” (ADMs) where the ADM of index 0 is the exact reduced density matrix. The equation of motion for the AMDs involves an infinite series of coupled differential equations of the form (in atomic units $\hbar = 1$):

$$\dot{\rho}_n = -i[H, \rho_n] - \sum_{m=0}^{M-1} \left(\sum_{k=0}^{\infty} n_{mk} \gamma_{mk} \right) \rho_n + \rho_n^{(+)} + \rho_n^{(-)} + T_n$$

See literature for the exact definitions and significance of the different terms in the equation above.

There are two main numerical paradoxes with the ADM equations of motion. Given that no computer can handle an infinite number of matrices, a truncation is required for the infinite series which is defined by the truncation parameter “L”. Additionally, the summation over the infinite set of Matsubara frequencies is truncated by its own parameter “K”. With a sufficiently large enough number of terms that survive the truncations, the equations of motion converge to the exact numerical reduced density matrix. The smallest set of truncation parameters will depend on the nature of the system. The truncation parameters should be chosen large enough to numerically converge to the correct solution, but not too large such that the computation becomes numerically unfeasible.

- Mini-Project Overview

The first goal of this mini-project is to calculate ET rate constants for a model spin-boson Hamiltonian and compare to the Marcus theory rate expressions with HEOM through the Libra software. The next step is to reproduce the results from Shi’s study on condensed phase electron transfer dynamics. Finally, the long-term goal is to use HEOM to solve the modified spin-boson model Hamiltonian we devised to test the capabilities of KC-RPMD in describing ET at electrode interfaces in condensed systems.

Methods:

Following the notation of Shi’s 2009 study, the spin-boson Hamiltonian to be solved with HEOM is:

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$H = V\hat{\sigma}_x - \frac{E_0}{2}\hat{\sigma}_z + \sum_j \frac{1}{2} \left[p_j^2 + \omega_j^2 \left(x_j - \frac{c_j}{\omega_j^2} \hat{\sigma}_z \right)^2 \right]$$

Where V is the electronic coupling between electronic states, and E_0 is the driving force.

Following the procedure carried out by Shi, the reduced density matrix was initialized propagated on the reactant electronic state with the electronic coupling set to zero. After a period of equilibration on the reactant electronic state, the Hamiltonian was updated to include off diagonal couplings and the rest of the dynamics were calculated. The harmonic equations of motion were solved with the Libra package framework. A small modification was made to the code to allow for the nuclear thermalization on the reactant electronic state. Specifically, the `libra_py.dynamics.heom.compute.run_dynamics` function was modified to split the timestep loop into two parts. The first part would run the dynamics using a Hamiltonian where the off-diagonal coupling elements were set to 0, at a specified timestep the first loop would terminate, the Hamiltonian would be updated to include the electronic coupling, and the remainder of the dynamics would be solved within the second loop.

The first calculation of the reduced density matrix was done at a temperature of $T = 300\text{ K}$, with a driving force of $E_0 = 0$, an electronic coupling of $V = 0.01 * \beta$, a reorganization energy of $\lambda = 0.01 * \beta$, and a cutoff frequency of $\gamma = 0.01 * \beta$. The convergence parameters were set to $L = 10$, and $K = 0$. A time step of $\Delta t = 5$ was used and the dynamics were run for a total of 10^6 steps with the thermalization period ending after 10^5 steps. Note all units are reported in atomic units. The resulting dynamics of the reduced density matrix are plotted in figure 1.

The second set of calculations solved for the reduced density matrix and was followed by a population analysis to calculate the rate constants at various driving forces $E_0 = 0 - 20$. The calculation was carried out at a temperature of $T = 300\text{ K}$, an electronic coupling of $V = 0.001 * \beta$, a reorganization energy of $\lambda = 10 * \beta$, and a cutoff frequency of $\gamma = 0.1 * \beta$. The convergence parameters were set to $L = 1$, and $K = 16$. A time step of $\Delta t = 0.5$ was used and the dynamics were run for a total of 5×10^5 steps with the thermalization period ending one quarter of the way in after 1.25×10^5 steps. Note all units are reported in atomic units. The ET rate constants were calculated from the HEOM trajectories as the negative average of the slope of the first diagonal entry of the reduced density matrix with the analysis starting three fourths into the trajectory which is halfway within the second half of the trajectory. Due to systematic disagreement with Marcus theory and the suspicion that much longer times are required to equilibrate the solvent, the ET rates are not reported here.

Results:

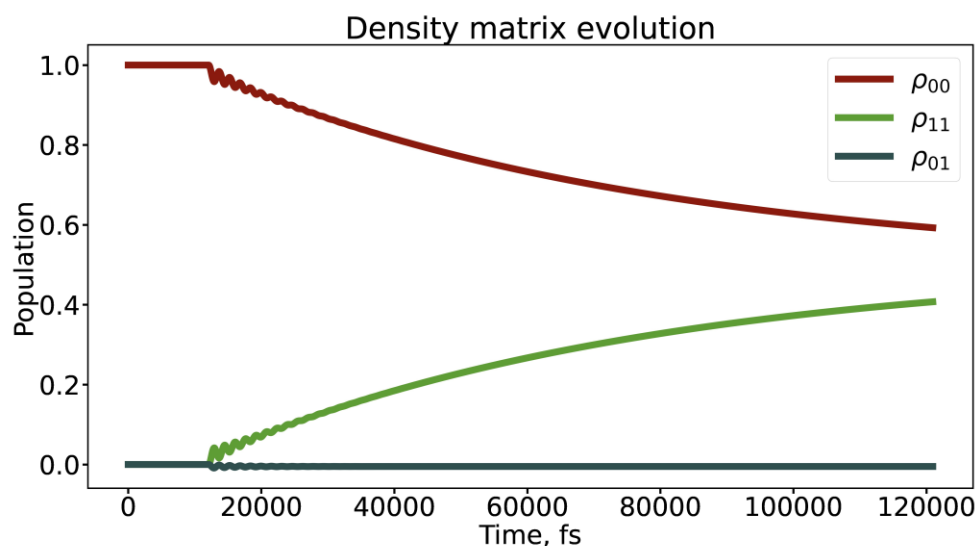


Figure 1. HEOM solution to density matrix following brief thermalization period. Parameters were set to $T = 300\text{ K}$, $E_0 = 0$, $V = 0.01 * \beta$, $\lambda = 0.01 * \beta$, and $\gamma = 0.01 * \beta$. The convergence parameters were set to $L = 10$, and $K = 0$.

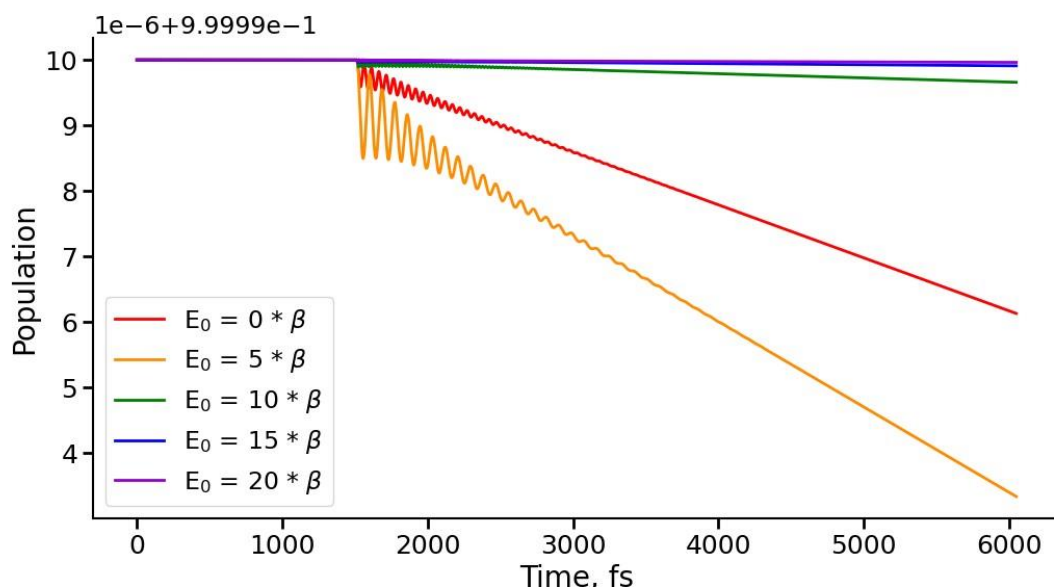


Figure 2. HEOM reactant state populations after a brief (yet relatively short) thermalization period as a function of driving force. Parameters were set to $T = 300 \text{ K}$, $V = 0.001 * \beta$, $\lambda = 10 * \beta$, and $\gamma = 0.1 * \beta$. The convergence parameters were set to $L = 1$, and $K = 32$.

Discussion and Conclusions:

In this mini project I got to explore HEOM and how it can be applied to solve electron transfer dynamics in condensed phase open quantum systems. In this brief period of time, I've gained an incredible amount of insight into the interplay between the solvation dynamics and electronic motions as well as the capabilities of HEOM as a method to describe these systems. Interestingly enough, these condensed phase systems with strong solvation coupling are the kinds of systems that HEOM struggles with the most to numerically converge, pushing the solvation parameters into the strong solvation region became a challenge as I had to balance between computational cost and capturing the desired physics. In particular, those Matsubara frequencies become a massive numerical bottleneck for HEOM with as few as $K = 3$ rendering some the calculations unfeasible in some cases. Nevertheless, it would seem as though these Matsubara frequencies are essential for describing solvation dynamics in these strong coupling condensed phase systems. The only reason I was able to get any calculations done in this regime within the time frame we had was because I chose an unrealistically small solvation cutoff frequency $\gamma = 0.1 * \beta$ which allowed the equations of motion to converge with a small number of ADMs, already converging at $L = 1$ allowing us to go up to $K = 64$ Matsubara terms. Despite its numerical challenges, the power of HEOM definitely lies in its accuracy and learning of its application to solve for ET rate constants will certainly prove useful for our group's research interests.

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