Optimal Control of Electron Transfer

by

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Abstract

We investigate a model that allows us to look at electron transfer in the fast-hopping regime. Using recent developments in the study of non-equilibrium processes, we compute optimal protocols which minimize the excess work required to drive the system from one control parameter value to another. Using these protocols, we evolve the system using Fokker-Planck dynamics to calculate how successful these protocols are over a variety of parameter values. We find that in using these protocols there is a trade-off between reducing the dissipation and successfully transferring the electron.

Keywords: Electron Transfer; Optimal Control; Fokker-Planck Dynamics

Dedication

For my parents Don and Karen Friesen.

Acknowledgements

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Chapter 1

Introduction

Our goal is to explore and develop theory on how to minimize the excess work done when trying to transfer an electron from one surface to another in non-equilibrium conditions. We examine the non-equilibrium thermodynamics of a simple model system that reflects the potential an electron may feel.

This topic may be of interest in a variety of fields. For example, in many fuel cells, electron-transfer e□ciency plays an important role. E□ciency is also important when designing solar cells or artificial photosynthesis. It may also have further application in biophysics in explaining how molecular machines achieve very high e□ciency, despite operating out of equilibrium.

A theoretical background will be described in Chapter 2 to flesh out the necessary details on optimal control of an out-of-equilibrium stochastic system.

1.1 The Model System

This section will cover the specifics of the model used [1]. We are interested in the transfer of an electron from one surface to another, such as from a metal to a molecule. We want to transfer the electron by ramping the potential voltage of one of the surfaces up or down appropriately in order to make it energetically favourable for the electron to be on one surface or the other. For the model, the two surfaces are described by two o□set quadratic traps. $V_0(x; \ )$ describes the system when the molecule is uncharged, and $V_1(x)$ describes the system when an electron has been transferred from the metal to the molecule:

$$V_0(x; \ ) = \frac{1}{2}k_0x^2 + \tag{1.1}$$

$$V_1(x) = \frac{1}{2}k_1(x - x_0)^2; \tag{1.2}$$

where is our time-dependent control parameter (the voltage) which we optimize, x_0 is some fixed distance between the surfaces, and the k's are the force constants of the traps.

We will make the approximation that we are in the fast-hopping regime. Then our electron is quickly switching between the distinct potentials $V_0(x; \ )$ and $V_1(x)$, and effectively sees a continuous potential of mean force (PMF) [2] defined by

$$E(x; \ ) = -\frac{1}{\ } \ln \ e^{\ V_0} + e^{\ V_1} \ ; \tag{1.3}$$

which is the Helmholtz free energy of the partition function summing over the two distinct potentials. Here, $\equiv (k_B T)^{\ 1}$ is the inverse temperature. The control parameter can take any value, but in the limit of large $|\ |$ the PMF approaches one of the distinct potentials (V_0 for negative and V_1 for positive). k_0 and k_1 can take any positive values, and we set x_0 and to unity.

Figure 1.1: PMF $E(x; \ )$ (black dashed curve) and distinct potentials $V_0(x; \ )$ (blue curve) and $V_1(x)$ (red curve), for $k_0 = 16{:}0$, $k_1 = 4{:}0$, and $= -2{:}0$.

Chapter 2

Theoretical Background

Fokker-Planck dynamics [3] describe a particle under the influence of drag and random forces, such as in Brownian motion. For any system that obeys Fokker-Planck dynamics,

for the generalized friction tensor

$$_{ij} \quad (t^0) \equiv \int_0^{Z\ 1} dt^{00}\, f_j(0)\, f_i(t^{00}) \quad _{(t^0)}: \tag{2.4}$$

$f_j(0)\, f_i(t^{00}) \quad _{(t^0)}$ is the force autocorrelation function, in terms of the equilibrium force fluctuations. The friction coefficient is indicative of the increase in energy cost of driving through parameter space quickly.

For potentials which satisfy $E(x; \ ) \Rightarrow \infty$ as $|x| \Rightarrow \infty$ it is possible [7], and much more convenient, to express the friction tensor in the form

$$_{ij}(\ ) = \frac{1}{D} \int_{1}^{Z\ 1} dx \frac{@_i \quad _{eq}(x; \ )@_j \quad _{eq}(x; \ )}{_{eq}(x; \ )}: \tag{2.5}$$

Here the components of the generalized friction are written entirely in terms of the equilibrium probability distribution $_{eq}$ and the equilibrium cumulative distribution function $_{eq}$ (both of which are analytic for our system), and a diffusion coefficient, which will be set to unity.

Our system only has a single control parameter , so the excess power and friction simplify to

$$P_{ex}(t^0) = \quad (\ (t^0)) \quad \frac{d}{dt} \quad ^2; \tag{2.6}$$

$$(\ ) = \frac{1}{D} \int_{1}^{Z\ 1} \frac{[@ \quad _{eq}(x; \ )]^2}{_{eq}(x; \ )}: \tag{2.7}$$

The average excess work is just the time integral of the average excess power

$$W_{ex} = \int_0^{Z} dt P_{ex}(t); \tag{2.8}$$

where is the duration of the protocol. We also have a generalized thermodynamic length

$$L \equiv \int_0^{Z} dt \quad q \overline{\quad\quad} P_{ex}(t): \tag{2.9}$$

We can place a lower bound on the excess work:

$$W_{ex} \geq \frac{L^2}{\quad}: \tag{2.10}$$

For the linear response approximation, by the Cauchy-Schwarz inequality the bound is only achieved by a protocol such that the excess power is constant over the protocol duration. We can solve the Euler-Lagrange equation, where the cost function $f(\ (t); \_) = \quad (\ )\_^2$ is

the excess power. This gives the solution

$$\_^{opt}(t) = \frac{(\ _f - \ _i)\ (\ (t))^{\ 1=2}}{R_0 \ dt\ (\ (t))^{\ 1=2}}\qquad (\ (t))^{\ 1=2}\ : \tag{2.11}$$

Put more intuitively, this shows that we would like to choose a path through parameter space where we are driving slowly when the friction coe□cient is large, and quickly when

Chapter 3

Results

3.1 Friction Coe□cient

approach the form of one of the distinct potentials, and changes in have little e□ect. In the large and equal k limit, the force variance approaches

$$f^2 = \frac{1}{4}\operatorname{sech}^2\frac{}{2}: \tag{3.5}$$

For $k_0 = k_1$, the fricti  respect to . For $k_0 = k_1$ the friction's d a negative for $k_0 > k_1$, and the friction is no longer symmetric about its maximum. In general, the friction peaks at larger values the larger the force constants are. This is also intuitive: as k increases, the force variance reaches some limit, but one would expect the relaxation time to continue increasing as the barrier between the wells continues to increase with k. Additionally, small values of do not significantly change the large barrier height, so we expect the relaxation time to be rela36 Td [(<xthe)-cs for

methods. We can rearrange Eq. (2.11) to get

$$t(\ ) = \frac{\int_{i}^{R} d\ p\ \overline{(\ )}}{\underline{+}\ 1\ R_{i}^{f} d\ p\ \overline{(\ )}}; \tag{3.6}$$

which is not a particularly enlightening form, but gives us expected behaviour as we drive quickly where the friction is small, and slowly where the friction is large.

Compared to a naive (straight-line) path, we want to drive our system quickly at the start and end of our protocol but more slowly in the middle.

3.3 Excess Work

Now that we know what our optimal path looks like, we can calculate the approximate excess work we do over the duration of our protocol, and compare it to the excess work we would do following a naive path. Although our previous expression for the path in Eq. (3.6) gives us the correct answer, we would prefer to have (t), rather than t( ). We achieve this by switching from an integral to a discrete step,

$$(t + \quad t) = \quad (t) + \frac{t \int_{i}^{R_f} d \; p \overline{\quad (\quad)}}{p \overline{\quad (\quad)}}; \tag{3.7}$$

which depends on our chosen protocol duration and endpoints. For sufficiently small t steps, we get the same paths we did previously using Eq. (3.6), and in a much more useful form.

We can now begin calculating the approximate average excess work, as well as run

The excess work is just the time integral of the excess power. Then the excess work is

$$\langle W_{ex} \rangle = \int_0 dt \; \left(\; (t)\right) \; \left(\frac{d}{dt} \right)^2 ; \tag{3.8}$$

which is approximated numerically by the sum

$$\langle W_{ex} \rangle = \sum_i \; t \; \left(\; (t_i)\right) \; \left(\frac{d}{dt} \right)^2_i ; \tag{3.9}$$

where $\left(\frac{d}{dt} \right)^2_i$ indicates the time derivative of the control parameter at a particular time t_i. There is some symmetry in the approximation of the excess work. Conjugate pairs of k, where the force constants are swapped (for example having parameters $k_0 = 4$ and $k_1 = 16$, then $k_0 = 16$ and $k_0 = 4$), will have the same excess work. This is due to our system having no preference (in the near-equilibrium limit) between going forward (driving from the left well to right well) and backwards (driving from the right well to left well). They are the same thing energetically, we just choose to go from left to right. Having $k_0 = a$ and $k_1 = b$ and going from left to right is the same situation as having $k_0 = b$ and $k_1 = a$ and going from right to left.

For the Fokker-Planck simulations, the work is

$$\langle W i \; !_i \quad _{i+1} = \int_1 dx \, [E(x; \; _{i+1} \quad E(x; \; _i)] \; \; (x); \tag{3.10}$$

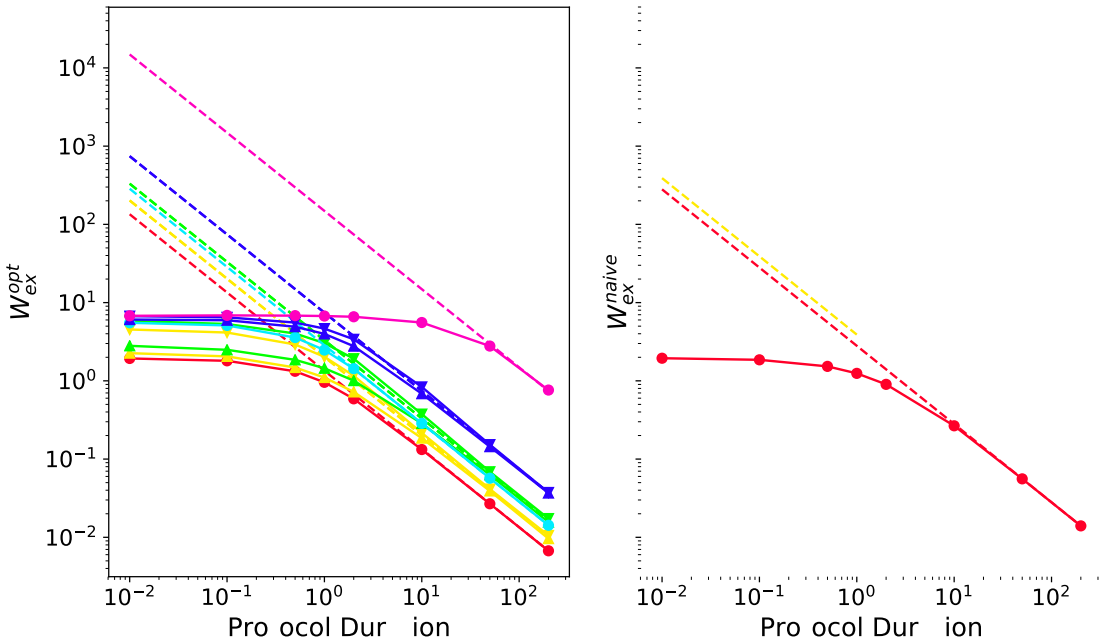
where (x) is the current probability distribution, which is generally not the same as the equilibrium distribution. Again, numerically we compute this as the sum

$$\langle W i \; !_i \quad _{i+1} = \sum_j \; [E(x_j; \; _{i+1}) \quad E(x_j; \; _i)] \; \; (x_j): \tag{3.11}$$

To go to the average excess work we sum over all steps in the protocol, minus the free energy, to get

$$\langle W_{ex} \rangle = \langle W \rangle \quad F: \tag{3.12}$$

The simulations act as expected in the long- and short-duration regimes. Generally, as the force constant of the traps increases, the excess work is increased. An interesting point is that although we start with our electron in the left well, where it is a ected mostly by k_0, the excess work for short durations depends more on k_1, shown by the grouping of the curves in Fig. 3.3. This is likely due to the probability distribution lagging far behind its equilibrium value for a particular along the protocol for short protocol durations. Because of the form of the PMF, as is increased, the PMF looks more and more like $V_1(x)$, and our electron, which has fallen behind due to the fast protocol, is farther from its equilibrium probability value. As our potential looks more like $V_1(x)$, it looks more likelooksit equ8.8m


W_{ex}^{opt}
10^{4}
10^{3}
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10^{-2}
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it, the points would converge. Unfortunately, this is difficult to continue due to increasing computational cost, both in calculating the optimal path on a finer time grid, and in solving the Fokker-Planck equation on a finer time grid and finer spatial grid.

Overall, for nearly any time, smaller k values allow a larger improvement in the amount of excess work done. The protocols with smaller k values approach their asymptotic limit more quickly (at a shorter protocol duration), and that limit is usually larger. In all cases, barring the case when $k_0 = 64$ and $k_1 = 16$, the optimal protocol successfully reduces the excess work done on the system. If the excess work is the primary concern in transferring our electron, the optimal path should be used in nearly all cases.

3.4 Distance from Equilibrium

The Kullback-Leibler divergence, also known as the relative entropy, is a measure of how one probability distribution is different from another reference probability distribution. We can use it as a measure of whether or not our protocol's succeed in getting the electron from the left well to the right well by comparing the final out-of-equilibrium distribution from the simulation to the equilibrium distribution expected for $_f$.

The relative entropy is defined as

$$D_{KL}(P \mid Q) \quad \sum_{x \in X} P(x) \ln \frac{P(x)}{Q(x)}; \tag{3.13}$$

where, in our usage, $P(x) = {}^{neq}_{f}(x)$ is the final probability distribution from the Fokker-Planck simulation, $Q(x) = {}^{eq}_{f}(x)$ is the equilibrium probability distribution for the system at the final control-parameter value of , and X is the system state space our distributions go over, which is the same for both of them. For our purposes, a smaller relative entropy is better, as it indicates the two distributions are more similar, and hence the protocol more successfully transfers the electron.

The relative entropy for several simulations are shown in Fig. 3.5, and the actual probability distributions are shown in Fig. 3.6. Again, at short protocol times, the results seem to be most strongly grouped by the k_1 value, rather than by k_0, even though the particle does not have a high probability of reaching the right well. Presumably, this is because k_1 has a dominant effect on the final equilibrium distribution we are comparing to. Similar to the ratio of the excess work, the relative entropy is best (lowest) when the force constants

Figure 3.5: Relative entropy at the conclusion of optimal (left) and naive (right) protocols, as a function of protocol duration. Circle markers indicate $k_0 = k_1$, up triangle markers indicate $k_0 > k_1$, and down triangle markers indicate $k_0 < k_1$.

distribution at equilibrium is very narrow. Because of how narrow the distribution is, the initial distribution is relatively farther out of equilibrium than for a case with a broader final equilibrium distribution. Because of how the relative entropy is defined, when we have a very narrow final equilibrium distribution, differences from it have larger contributions to

Chapter 4

Methods

Most of the programming for this project was done in FORTRAN. The only exception was the code used for the Fokker-Planck equation, which was adapted from existing code written in Cython, which was developed by Joseph Lucero.

4.1 Integration

Because of the simple form of the model, many functions had a closed-form expression. For those that did not, numerical methods were used.

Many of the expressions for quantities we were interested in included integration from negative to positive infinity. If there was no analytic solution, in order to make the problem tractable, we selected an appropriate range over which to integrate. For integration over , the canonical ensemble for the system was used to find the probability of being on the potential V_0 or V_1, as appropriate. Taking $V_0(x;)$ and $V_1(x)$ as the energy states of the system, we can then integrate out x by taking

$$U( ) = \frac{-1}{} \ln \int_{1}^{Z_{1}} dx e^{V} ; \tag{4.1}$$

where just labels the potential we are currently working with. Because the individual potentials are simple quadratic wells, these are just Gaussian integrals with analytic solutions. Additionally, V_1 is independent of , so this expression will just give a constant. We can then find our probability of being on one potential or the other by taking

$$= \frac{e^{U}}{e^{U_0} + e^{U_1}}: \tag{4.2}$$

range is skewed towards the tighter trap. For example, for $k_0 < k_1$ the range will shift to more positive values.

We do something similar when trying to find a reasonable x range to integrate over. In this case, we look to our analytic solution for the probability distribution. We are interested in an x range where the probability of finding our particle is greater than some tolerance, and also contains both wells (we don't stop at the low probability at the energy barrier). We can find where the probability distribution gets sufficiently small by using bisection [8]. We bracket an interval $(a; b)$ such that $f(a)$ has a value greater than our desired tolerance, and $f(b)$ has a value less than our desired tolerance. Using bisection we can find, to machine precision, where our probability distribution is equal to our desired tolerance. As long as our initial guess for a and b bracket our desired tolerance, the bisection method can not fail. Using this method we find out how far we must integrate over x before the probability of

conditions and a guess of the solution. In order to apply the FTCS method, we must discretize the derivatives in Eq. (4.3). The FTCS scheme is first order in time, and second order in space. Then the obvious way to discretize the derivatives is to set

$$\frac{@}{@t}(x;t) \approx \frac{(x;t+\quad t)-\quad (x;t)}{t}; \tag{4.4a}$$

$$\frac{@}{@x}[\ (x;t)\ \ (x;t)] \approx \frac{(x+\quad x;t)\ \ (x+\quad x;t)-\quad (x;t)\ \ (x;t)}{2\quad x}; \tag{4.4b}$$

$$\frac{@^2}{@x^2}[D(x;t)\ \ (x;t)] \approx D(x+\quad x;t)\ \ (x+\quad x;t)-2(x;t$$

One may also consider discretizing the probability flux and setting it to zero, where the flux is obtained by solving

$$\frac{@}{@t} = -\frac{@J}{@x} \tag{4.7}$$

where J is the flux. This gives us

$$J = \quad -\frac{@}{@x}(D \quad): \tag{4.8}$$

Discretizing this and setting it to zero at the boundary, we get

$$0 = \quad _0 - D \quad \frac{_0 - \quad _1}{x} \quad ; \tag{4.9a}$$

$$_1 = \quad _0 \quad \frac{x}{D} - 1 \quad ; \tag{4.9b}$$

for the left boundary, which is still not good enough. The probability is still able to leak out of the simulation box. However, if we apply bot

Chapter 5

Conclusions

This research explored how to transfer an electron or other particle from one surface to another out of equilibrium while minimizing the amount of excess work done. To this end, a simple model was developed, using two quadratic potential wells to simulate the two surfaces. We made the assumption that we were operating in the fast-hopping regime, where we could treat the two distinct potentials as one continuous one. We calculated the general friction tensor, and used it to calculate an optimal path through parameter space that should require the least excess work. We then simulated the evolution of the probability distribution using the Fokker-Planck equation. From these simulations we were able to calculate the excess work, and we were able to calculate the relative entropy by comparing the final non-equilibrium distribution to the expected equilibrium distribution.

Our results suggest that there is a trade-o between optimizing for reduced excess work, and how fast one is able to have a high chance of successfully transferring the electron. In nearly all cases, excluding some for short protocol times, the calculated optimal protocol required less excess work than the naive straight line protocol. This can be seen most clearly in Fig. 3.4, where the ratios of the excess works for naive and optimal protocols are shown. As may be intuitive, more loosely bound electrons (represented by smaller force constants) allow for greater excess work savings, and we can reach the asymptotic limit of these savings in a shorter protocol duration. Conversely, the distance from equilibrium at the conclusion of the protocol (quantified by the relative entropy, shown in Fig. 3.5) was higher for the optimal protocol compared to the naive protocol for equal duration. This indicates that the final non-equilibrium probability density of the optimal protocol was not as similar to the desired equilibrium probability density as was its naive counterpart. Using the optimal protocol generally results in excess work savings, but has a reduced chance of successfully transferring the electron in a given protocol time.

5.1 Future Work

For future works continuing this research we would like to improve the precision of our simulations. This would be best done by changing our method of solving the Fokker-Planck equation, as well as how we input protocols. At the time of writing, the protocol was calculated and written to file so that they would be reusable. For increased precision, it is necessary to reduce the time step between points on the protocol. Gaining high precision means very small time steps (which results in very large files) and long run times. Moving forward, it may be beneficial to compute the path one step at a time, as the simulation runs, to keep the memory cost manageable. Additionally, we could move to more sophisticated methods, such as implicit methods. Although the FTCS algorithm works, it is not particularly stable. Implicit methods would allow better stability, putting less constraints on the timestep size we use when integrating.

Aside from programming improvements, we would also like to explore other aspects of the system. In this instance we operated in the fast-hopping regime, where we smoothed our two distinct potentials into one continuous one. Alternatively, we could leave the potentials as distinct, and describe the transfer of electrons through a hopping probability such as $_{0\Rightarrow 1} = \frac{t}{\sim} f(E(x;t))$ for transfer from the left well to the right well, and $_{1\Rightarrow 0} = \frac{t}{\sim}(1 - f(E(x;t)))$ for transfer from the right well to the left well, where $f(E(x;t))$ is the Fermi function, $E(x;t)$ is the energy difference between the distinct potentials, and $$ is a constant which describes the electron coupling, which is independent of the energy gap.

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