1 Background

1.1 Marcus Hopping

Starting with Fermi's Golden Rule, the transfer rate between some initial and final state can be found [1, 2, 3]:

$$\nu_{if} = \frac{|t_{if}|^2}{\hbar^2} \int_0^\infty dt \cos\left(\sum_j S_j \sin\omega_j t\right) e^{-\sum_j S_j(2n_j+1)(1-\cos\omega_j t)}, \tag{1}$$

where t_{if} is the transfer integral and $S_j = \lambda_j/\hbar\omega_j$ and $n_j = [e^{\hbar\omega_j/k_BT}-1]^{-1}$ are the Huang-Rhys factor and population of the j^{th} normal vibrational mode. In either the strong coupling limit ($\sum_j S_j \gg 1$) or the high temperature limit ($k_BT \gg \hbar\omega_j$ for dominant vibration modes), this expression simplifies to [4]

$$\nu_{if} = \frac{|t_{if}|^2}{\hbar^2}\sqrt{\frac{2\pi}{\sum_j S_j\omega_j^2(2n_j+1)}} e^{-\frac{(\omega_{if}+\sum_j S_j\omega_j)^2}{2\sum_j S_j\omega_j^2(2n_j+1)}}. \tag{2}$$

In the high-temperature limit, this reduces to the Marcus hopping rate equation [5]:

$$\nu_{if} = \frac{|t_{if}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_BT}}\, e^{-\frac{(\Delta G_{if}+\lambda)^2}{4\lambda k_BT}}, \tag{3}$$

with $\Delta G_{if} = \hbar\omega_{if}$ the change in Gibbs free energy between the two configurations and $\lambda = \sum_j S_j\hbar\omega_j$ the so-called "reorganization energy" associated with effort needed to undergo the state transition.

1.2 Dangling Bond Hopping Model

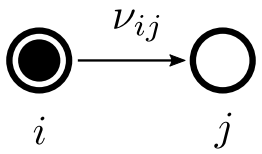

Figure 1: A single electron hops between two DBs with a transfer rate given by Marcus Theory.

Consider two dangling bonds which share an electron. According to Marcus Theory, the electron hops between the two DBs with a transfer rate:

$$\nu_{ij} = \frac{|t_{ij}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_BT}} e^{-\frac{(\Delta G_{ij}+\lambda)^2}{4\lambda k_BT}} \tag{4}$$

where

$$\begin{aligned} t_{ij} &: \text{electron transfer integral} \\ \lambda &: \text{reorganization energy; self-trapping energy} \\ \Delta G_{ij} &: \text{change in Gibbs free energy for the electron transfer} \end{aligned}$$

The transfer integrals arise from the DB orbital overlap and can be assumed to be a function only of the DB arrangement and fixed throughout the surface simulation. The reorganization energy

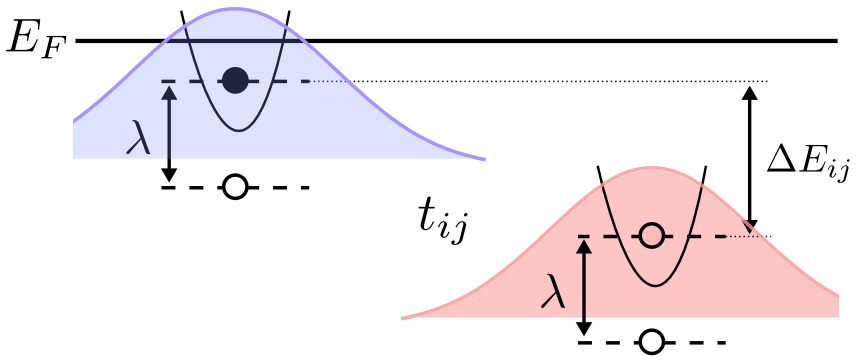

Figure 2: Each DB is modelled as a well with a single bound state. When a DB contains an electron, that electron is self-trapped with a given energy λ. The energy level of each well is determined by the local potential at that well arising both from external fields such as those from the tip and from Coulombic interactions between occupying electrons. The wavefunction overlap between the wells gives the transfer integrals.

is a fixed property of the lattice and is identical for all DBs. Each of the DBs is identical so the change in Gibbs free energy arises only from the occupation energy of each DB: $\Delta G_{ij} \approx \Delta E_{ij}$. The energy of a charge configuration $\vec{n}$ is of the form

$$E(\vec{n}) = -\sum_i U_i n_i + \frac{1}{2}\sum_{<i,j>} V_{ij} n_i n_j = -\vec{U}^T\vec{n} + \frac{1}{2}\vec{n}^T V \vec{n} \tag{5}$$

where n_i is the number of electrons at the i^{th} site, U_i is the local potential due to external fields such as those from the tip, and V_{ij} is the strength of the Coulombic interaction between each site. We approximate any potential Debye screening by using an interaction of the form

$$V_{ij} = \frac{q}{4\pi\epsilon r_{ij}} e^{-r_{ij}/\lambda_D} \tag{6}$$

with r_{ij} the distance between DBs and λ_D the Debye length.

1.3 Hopping Intervals

For a given hopping rate ν, we should expect a hop to occur after $\langle\tau\rangle = \nu^{-1}$ seconds, where τ is the hopping interval. If ν is fixed, τ is an exponential random variable with probability $P(\tau \leq t) = 1 - e^{-\nu t}$. We can interpret the transfer dynamics in two ways:

1. a hop is attempted after some τ seconds with $P(\tau \leq t) = 1 - e^{-\nu t}$.
2. a hop is attempted after some τ_0 "ticks" with $P(\tau_0 \leq t) = 1 - e^{-t}$ and a "tick rate" of ν ticks per second.

This tick rate picture is convenient as it naturally leads to the behaviour for an electron among multiple DBs. Each possible hopping destination contributes ν_{ij} to the rate at which the electron "leaks" out of its current DB. Therefore, a hop occurs after τ_0 ticks with the tick rate given as $\nu_i = \sum_j \nu_{ij}$. Further, the ν_{ij} can be time varying without any challenge (see Appendix A). We refer to τ_0 as the *lifetime* of a charge.

1.4 Marcus-Boltzmann Distribution

After τ seconds, an electron hops from site i to some target j. The probability of hopping to j is proportional to ν_{ij}:

$$p_{ij} = \alpha\nu_{ij} = \frac{\nu_{ij}}{\sum_k \nu_{ik}} \tag{7}$$

The form of this distribution has similar properties to the Boltzmann distribution. Namely, the hopping probability is highly affected by the resulting change in energy. For that reason, this distribution will be referred to as the Marcus-Boltzmann distribution:

$$p_{ij} = \frac{|t_{ij}|^2 e^{-\frac{(\Delta E_{ij}+\lambda)^2}{4\lambda k_B T}}}{\sum_k |t_{ik}|^2 e^{-\frac{(\Delta E_{ik}+\lambda)^2}{4\lambda k_B T}}}$$

Question: is this necessarily true? For time varying ν_{ij} it might make more sense that the probability be something more like

$$p_{ij} = \frac{\int_0^\tau \nu_{ij}(t)dt}{\sum_k \int_0^\tau \nu_{ik}(t)dt}$$

as this would give the weighted accumulated charge leakage to each possible hopping target rather than using only the instantaneous rates. However, this might result in charges hopping to sites which recently became unfavourable due to other hopping events. Also there are issues: what if most of the charge leakage (consumption of τ_0) was to a DB which was later occupied and hence no longer available?

2 Numerical Details

Recall that the energy associated with a charge configuration is given as

$$E(\vec{n}) = -\vec{U}^T\vec{n} + \frac{1}{2}\vec{n}^T V \vec{n}.$$

An electron now tunnels from site i to j: $\delta\vec{n} = \vec{n}' - \vec{n} = \hat{e}_j - \hat{e}_i$. Assuming $\vec{U}$ is independent of the charge state, the change in energy is computed as

$$\Delta E_{ij} = E(\vec{n}') - E(\vec{n}) = -\vec{U}^T\delta\vec{n} + \frac{1}{2}\left[\vec{n}'^T V\vec{n}' - \vec{n}^T V\vec{n}\right] = -[\vec{U} - V\vec{n}]^T\delta\vec{n} - V_{ij}.$$

If we define $\vec{\epsilon} = \vec{U} - V\vec{n}$, we obtain the convenient expression:

$$\Delta E = \hat{\epsilon} \otimes \hat{1}^T - \hat{1} \otimes \hat{\epsilon}^T - V \tag{8}$$

where ΔE is the matrix of all possible energy changes for the current charge state. Note that either Python or MATLAB will do the broadcasting for free so this is simply $\Delta E = \vec{\epsilon} - \vec{\epsilon}^T - V$. One important efficiency note here is that for a charge state with N electrons among M DBs, there are only N rows (hopping sources) and $M - N$ columns (hopping targets) that are relevant to the calculations. If we slice $\vec{\epsilon}$ and V appropriately, we only ever have to deal with a ΔE of size $N \times (M - N)$.

3 Current Questions

3.1 Tip Model

The tip induces an effective change in the local potentials at each site. This potential is a function of the current charge configuration and so cannot simply be considered an additional term in $\vec{U}$ like other external fields. There is no real obstacle to simply extending the interpretation of $\vec{U}$. We can generalise the ΔE_{ij} equation as follows:

$$\Delta E_{ij} = -[\vec{U}' - V\vec{n}]^T \delta\vec{n} - V_{ij} - \Delta\vec{U}^T\vec{n} \tag{9}$$

where $\vec{U}' = \vec{U}(\vec{n}')$ is the vector of local potentials after the hop, and $\Delta\vec{U} = \vec{U}' - \vec{U}$. For every i and j there is new $\vec{U}'$ and so we can't do any additional tricks without more information: i.e. how much can the tip model be parametrized, how many states do we expect to see near equilibrium (store tip influence for each state in a look-up table), etc.

3.2 Population

The current implementation of the Marcus simulator fixes the number of electrons. Nothing regarding the Fermi level is considered. One simple approach which could be easily implemented is to add an additional hopping channel to/from a reservoir. The effective potential experienced at each DB is given as

$$\vec{U}_{eff} = \vec{U} - V\vec{n} \tag{10}$$

This is of course equal to $\vec{\epsilon}$ from before. This is a measure of the absolute energy of the bound state of each well. There is a transfer rate from all occupied DBs **to** the reservoir and **from** the reservoir to all empty DBs. This rate is a function of $\vec{U}_{eff}$. It is just a matter of finding the right parameters to match experiment.

A Validation of the Tick-Rate Interpretation

Given some time varying transfer rate $\nu(t)$, the probability of a hopping event occurring in some small time dt is given by

$$p(t) = \nu(t)dt. \tag{11}$$

The hopping interval, i.e. the time until the first hopping event, is found to have probability

$$P(\tau \leq t) = 1 - e^{-\int_0^t \nu(t')dt'}. \tag{12}$$

Suppose we generate some exponential random variable τ_0 according to

$$P(\tau_0 \leq t) = 1 - e^{-t} \tag{13}$$

and at each instant in time, we decrement τ_0 by $\nu(t)dt$. The time, τ, until τ_0 is depleted is given implicitly as

$$\tau_0 = \int_0^\tau \nu(t)dt. \tag{14}$$

We are interested in the quantity $P(\tau \leq t)$. If we assume $\nu(t) > 0$ then $\tau \leq t$ is equivalent to $\int_0^\tau \nu(t')dt' \leq \int_0^t \nu(t')dt'$. It follows then that

$$P(\tau \leq t) = P\left(\tau_0 \leq \int_0^t \nu(t')dt'\right) = 1 - e^{-\int_0^t \nu(t')dt'} \tag{15}$$

So τ has exactly the correct statistics. Note that on generating τ_0 we knew nothing about the future values of $\nu(t)$. By consuming τ_0 at the current $\nu(t)$, we effectively have generated the waiting time consistent with the future transfer rates. Therefore any change to the future charge state (and transfer rates) is automatically accounted for.

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