# SUPPLEMENTAL INFORMATION

# Catalytic Resonance Theory: Forecasting the Flow of Programmable Catalytic Loops

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Section S1. Binding Energies Derivation

## Binding Energies Derivation

Linear scaling relationship between changes in binding energies of two species are defined by two parameters gamma and delta. Between species A and B, these parameters are

$$\gamma_{B-A} = \frac{\Delta BE_B}{\Delta BE_A} \qquad \text{(S1.1)}$$

$$\delta_{B-A} = H_A^*|_\delta = H_B^*|_\delta \qquad \text{(S1.2)}$$

Such that when $BE_A = \delta_{B-A}$, $BE_B = \delta_{B-A} + \Delta H_{rxn}$, where $\Delta H_{rxn}$ is the overall heat of reaction.

Integration of equation S1.1 yields:

$$BE_B = \gamma_{B-A} BE_A + C \qquad \text{(S1.3)}$$

Upon substitution of $BE_A$ and $BE_B$ from the case of equal surface enthalpies, the constant of integration is achieved:

$$C = (1 - \gamma_{B-A})\delta_{B-A} + \Delta H_{rxn} \qquad \text{(S1.4)}$$

Substituting S1.4 into S1.3 defines the binding energy of species B in relation to the binding energy of species A.

$$BE_B = \gamma_{B-A}\, BE_A + (1 - \gamma_{B-A})\, \delta_{B-A} + \Delta H_{rxn} \qquad \text{(S1.7)}$$

Which for a thermoneutral reaction simplifies to:

$$BE_B = \gamma_{B-A}\, BE_A + (1 - \gamma_{B-A})\, \delta_{B-A} \qquad \text{(S1.8)}$$

In a similar derivation, as adapted from Gathamann et. al[2], as $\Delta BE_X$ describes a perturbation to the binding energy of species X, the relationship defining $\gamma_{B-A}$ can be rewritten as:

$$\gamma_{B-A}\left(BE_{A,1} - BE_{A,2}\right) = \left(BE_{B,1} - BE_{B,2}\right) \qquad \text{(S1.9)}$$

Describing state 2 as the catalytic state in which the two surface species have equivalent surface enthalpies, $BE_{A,2}$ and $BE_{B,2}$ can be rewritten as the change in enthalpy upon that species binding to the catalyst.

$$\gamma_{B-A}(BE_A - (H_A - H_A^*|_\delta)) = (BE_B - (\, H_B - H_B^*|_\delta)) \qquad \text{(S1.10)}$$

$$\gamma_{B-A}(BE_A - (H_A - \delta_{B-A})) = (BE_B - (H_B - \delta_{B-A})) \qquad \text{(S1.11)}$$

Rearranging equation 11 gives:

$$BE_B = \gamma_{B-A}\, BE_A - \ (1 - \gamma_{B-A})\, \delta_{B-A} + (H_B - \gamma_{B-A} H_A) \qquad \text{(S1.12)}$$

Simplifying for a thermoneutral reaction causes the final term in parenthesis to drop out yielding,

$$BE_B = \gamma_{B-A}\, BE_A - \ (1 - \gamma_{B-A})\, \delta_{B-A} \qquad \text{(S1.13)}$$

Upon inclusion of this binding energy relationship with the functions of my code, I experienced back and forth switching between the two to determine whether the + or – sign preceding $(1 - \gamma_{B-A})\, \delta_{B-A}$. It was found that a + sign is consistent with thermodynamic expectations. In equation 13, a gamma value of less than 1 often yields a negative value for $BE_B$, which is inconsistent with the positive definition of binding energies. Equation 13 only upholds with thermodynamic expectations if binding energies are described as equivalent to the enthalpy of adsorption rather than the mathematical inverse of the enthalpy of adsorption.

Section S2. Microkinetic Model Derivation

**Activation Energies**

The Bronsted-Evans-Polanyi relationship is used to define the activation enthalpy of the forward direction of each unimolecular elementary step, which assumes a linear correlation between the activation energy and the heat of surface reaction. This relationship takes on the form,

$$E_a = \alpha \Delta H_R + \beta \qquad \text{(S2.1)}$$

**Rate Constants**

Computation of the forward rate constants involves the computed activation energies and [re-exponential factors derived from transition state theory, assuming a transition coefficient of 1, such that the pre-exponential is $\frac{k_B T}{h}$, computed at the chosen reaction temperature. For the first elementary reaction, the forward rate constant is defined as,

$$k_1 = \frac{k_B T}{h} exp\left[-\frac{Ea}{k_B T}\right] \qquad \text{(S2.2)}$$

Equilibrium constants arise from the definition of thermodynamic equilibrium, and the reverse rate constant is yielded from the forward rate constants and the equilibrium constant to yield thermodynamic consistency. For the model used in this work, the entropy change for the surface reaction is assumed to be negligible relative to the heat of surface reaction.

$$K_1 = exp\left[-\frac{\Delta G}{k_B T}\right] = exp\left[-\frac{(BE_B - BE_A) + T\Delta S}{k_B T}\right] \qquad \text{(S2.3)}$$

$$k_{-1} = \frac{k_1}{K_1} \qquad \text{(S2.4)}$$

At each catalyst state, in accordance with the principle of microscopic reversibility, it also stands that, $k_3 k_2 k_1 = k_{-1} k_{-2} k_{-3}$, which yields the following reciprocal relationship at equilibrium,

$$1 = K_1 K_2 K_3 = \left(\frac{k_1}{k_{-1}}\right)\left(\frac{k_2}{k_{-2}}\right)\left(\frac{k_3}{k_{-3}}\right) \qquad \text{(S2.5)}$$

**Species Balances**

Rate equations were formulated for each elementary step, in accordance with mass-action kinetics. As this model only accounts for the conversion on the surface of the catalyst, the total surface coverage is set as a constant.

$$\theta_{species} = 1 - \theta^* = \theta_A + \theta_B + \theta_C \qquad \text{(S2.6)}$$

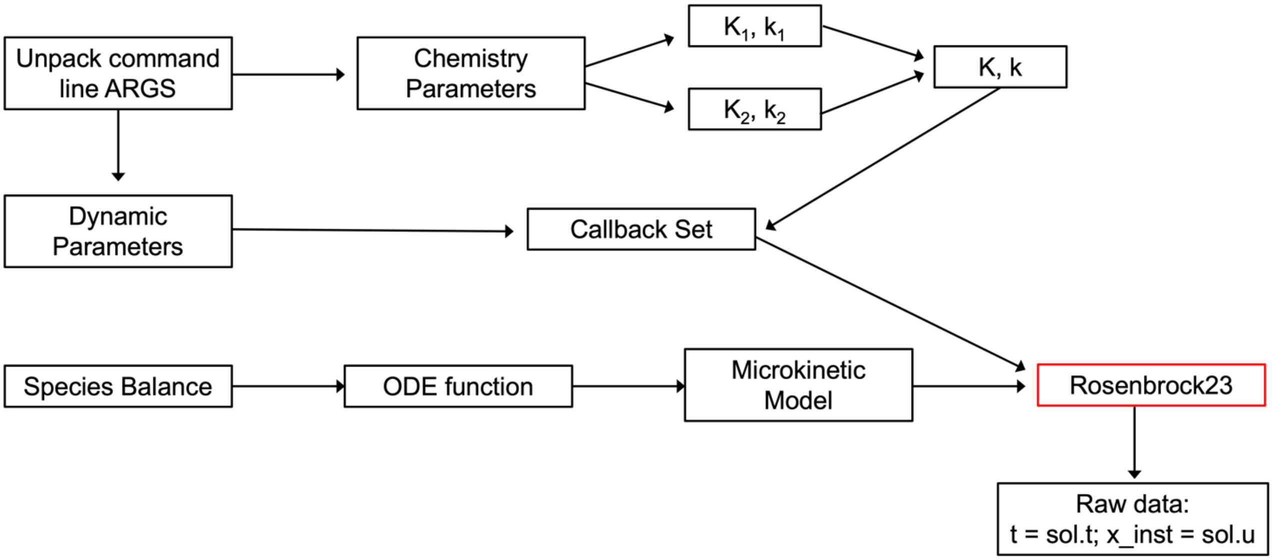
$$\frac{d\theta_A}{dt} = -r_1 + r_2 = k_3\theta_C + k_{-1}\theta_B - (k_1 + k_{-3})\theta_A \qquad \text{(S2.7)}$$

$$\frac{d\theta_B}{dt} = -r_2 + r_3 = k_1\theta_A + k_{-2}\theta_C - (k_2 + k_{-1})\theta_B \qquad \text{(S2.8)}$$

$$\frac{d\theta_C}{dt} = -r_1 + r_2 = k_2\theta_B + k_{-3}\theta_A - (k_3 + k_{-2})\theta_C \qquad \text{(S2.9)}$$

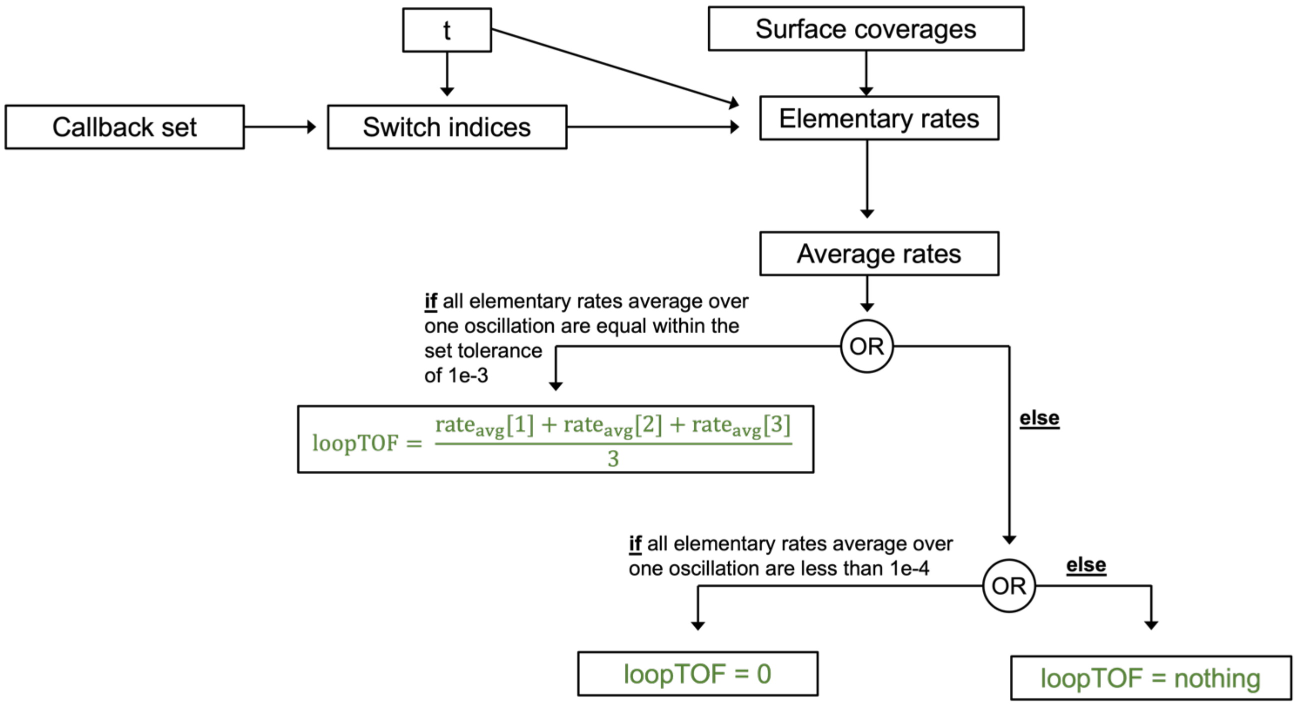
Section S3. Code Development and Block Logic Diagrams

### Integration Block Logic Diagram: Dynamic Loop Simulation



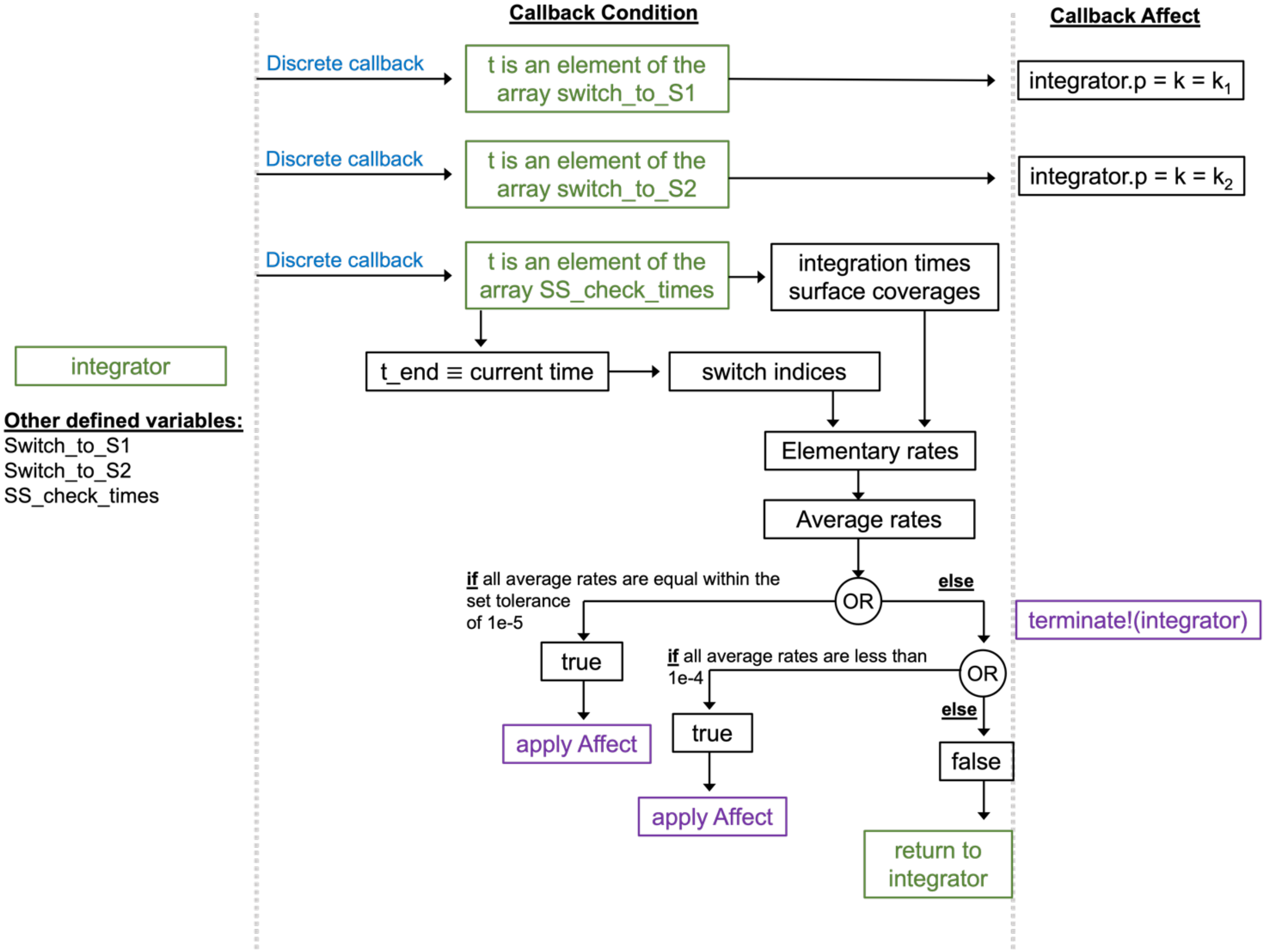
The choice of using Rosenbrock23 over other ODE solvers is outlined in Section S.3. See the LoopSimulation.jl, Callbacks.jl, and CycleBaseFuncts.jl for the functions and code that implements the integration logic diagram. The diagram outlines the preprocessing of chemistry parameters to generate the one input parameter for the integrator, the array of rate constants, k. The diagram also outlines the transformation of the species balances into a microkinetic model that can be solved by the ODE solver. The output of the solver is the raw data for the time and surface coverages of species A*, B*, and C*.

### Output Analysis Block Logic Diagram: Dynamic Loop Simulation



The output analysis block logic diagram outlines the progression from the raw data form time (t) and surface coverages to the final output of loop turnover frequency. The choice to cutoff round loop turnover frequencies under 1e-4 to 0 was made for two key reasons. The first being the computational time required by each simulation. Rounding down allowed simulations to be terminated early once the time-averaged elementary rates over one oscillation were less than 1e-4, preventing the need for further integration, effectively saving computational time and resources when running simulations. Furthermore, for the purpose of using machine learning to analyze the bank of results, the data with a zero loop turnover frequency needed to be separated from the data with a non-zero loop turnover frequency. To prevent overfitting of the data, 1e-4 was recognized as a small loop turnover frequency, representing negligible motion of the surface species about the loop and therefore, all outputs of a net loop turnover frequency less than 1e-4 in magnitude were rounded down to zero.

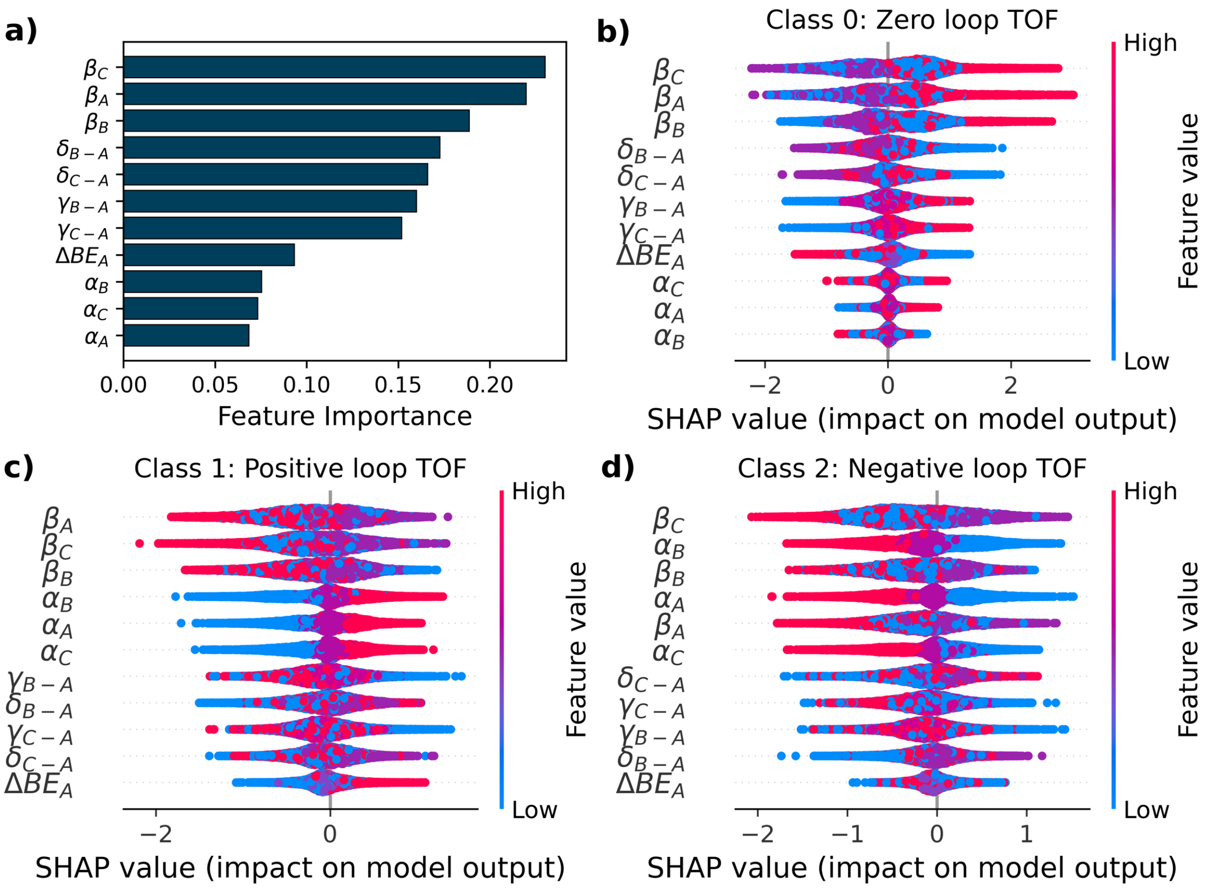
## Callback Set: Dynamic Loop Simulation



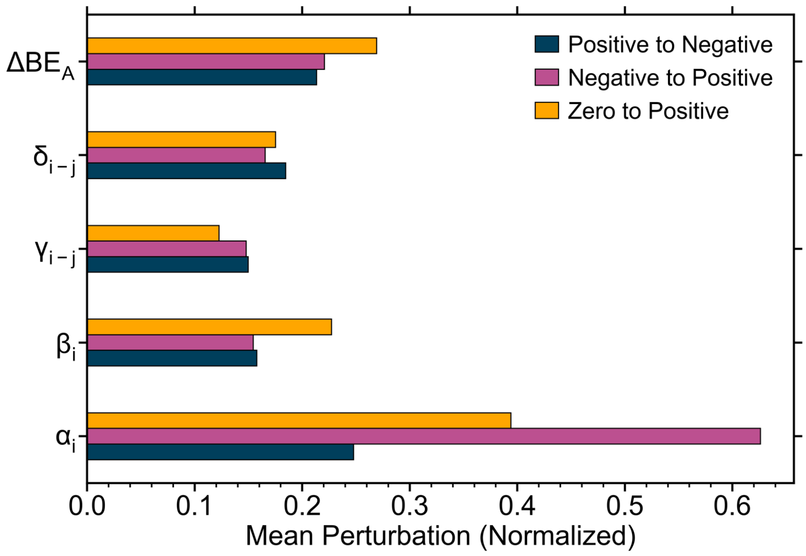
The callback set block logic diagram identifies when certain callbacks are called, based on their callback condition, and the affect it employs on the integrator. In the first callback, when the time, t, exhibits a time in the array holding the times to switch to state 1, the integration parameter (rate constant array, k) is set to k1$_1$. Similarly, when the time agrees with an element in the switch to state 2 array, the integration parameter is set to $k_2$.

The final callback set is used to check if the integration has reached steady state. The integration checks for steady state once the time is an element of the array with steady state check times. This array includes the entries in switch_to_S1, but only for every 10 oscillations. The callback function extracts the time data and surface coverage data from the previous integration and determines the switch indices. Those arrays are utilized to compute the instantaneous elementary rates which are then averaged over the past 2 oscillations. If all of the time-average rates are equal within the set tolerance of 1e-5 then steady state has been reached and the affect is applied. If all the time average rates are less than 1e-4 than the loop turnover frequency is effectively zero and further integration is no longer needed so the affect is applied. If neither of those are true, the callback function returns false and integration proceeds. The callback affect is the termination of the integrator.

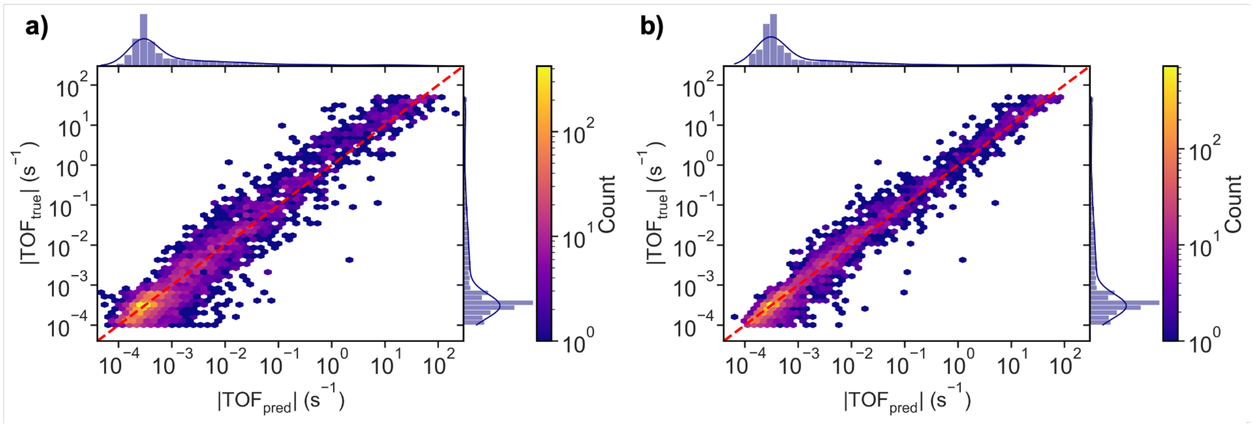
All the callbacks employed are discrete callbacks, meaning that the callback is applied with the condition function is true, but the condition function is only evaluated at the end of each integration step.



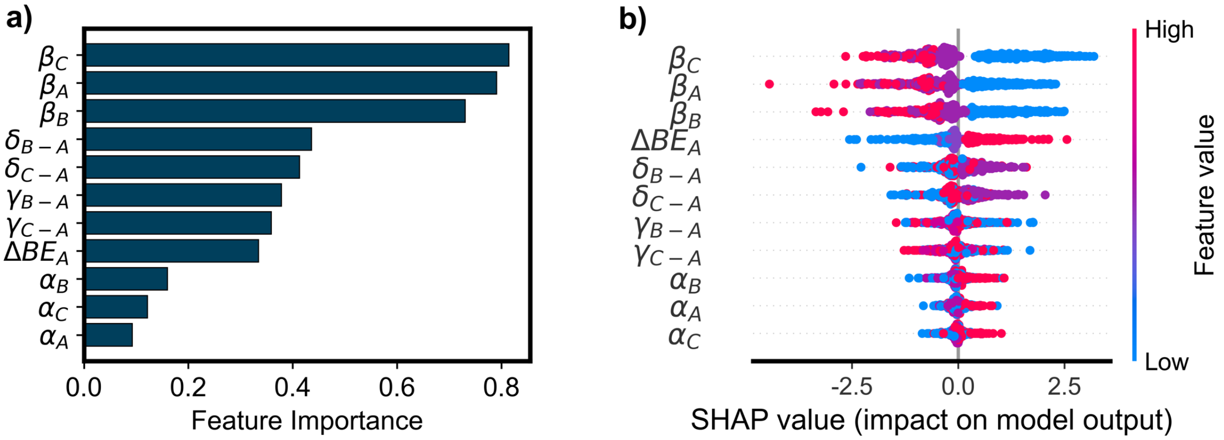
**S4. Permutation Feature Importance and SHAP Analysis of the XGB-OP Classifier. (a)** Permutation feature importance (PFI) analysis on the XGBoost original parameter (OP) classification model. **(b-d)** SHAP analysis on the OP classifier for each class: **(b)** zero TOF, **(c)** positive TOF, **(d)** negative TOF.



**S5. Counterfactuals of the XGB-OP Classifier Model.** Counterfactuals explorations for three class switches in the XGB-OP classifier model. The perturbation to each feature was averaged over all samples, then averaged across each type of feature (e.g., $\alpha_i$ includes perturbations to $\alpha_A$, $\alpha_B$, and $\alpha_C$).



**S6. Parity Plots for the XGB Regressors. (a)** The XGB-OP Regressor model predictions. **(b)** The XGB-RC Regressor predictions. The red dashed line indicates a perfect 1:1 correlation while the color indicated density of points. Density is also indicated by the histograms on either axis.



**S7. Permutation Feature Importance and SHAP analysis on the XGB-OP Regressor model.** **(a)** Permutation feature importance (PFI) analysis on the XGBoost original parameter (OP) regressor model. **(b)** SHAP analysis on the XGBoost OP regressor.