Abstract

It has long been known that non-steady state and periodic catalytic reactor operation in temperature, pressure, and composition can lead to higher overall productivity or product selectivity than the best steady operation. Recently, the emergence of catalysts whose intrinsic properties can oscillate with time introduces novel forcing capabilities that can be “programmed” into the catalysts, so to broaden the scope and applicability of periodic operation to surface chemistry. In this work, an algorithmic approach was implemented to significantly accelerate the discovery and optimization of periodic steady states. Decomposition of complex dynamics into fundamental mechanistic fast-slow steps improves conceptual understanding of the relationship between binding energy oscillation protocols and overall catalytic rates. Finding the structured forcing protocols, optimally tailored to the multiple time scales of a given individual mechanism, requires efficient search of high-dimensional parameter spaces. This is enabled here through active learning (Bayesian Optimization enhanced by our proposed Bayesian Continuation). Implementation of these methods is shown to accelerate the evaluation of catalyst programs by up to several orders of magnitude. Faster screening of programmable catalysts to discover periodic steady states enables the optimization of catalytic operating protocols; it thus opens the possibility for catalyst engineering based on optimal forcing programs to control rate and product selectivity, even for complex multi-step catalytic mechanisms.

Keywords: Catalysis, Heterogeneous Catalysis, Dynamics, Programmable, Optimization.
1 Introduction

Rate enhancement of heterogeneous catalytic reactors remains a focus of chemical research in academia and industry, as it translates to reduction in costs and environmental footprint [1]. It is particularly relevant to the challenges of sustainability (e.g. carbon dioxide as feedstock [2, 3, 4], pollutant degradation [5, 6]), basic chemicals production (e.g. ammonia [7, 8], monomers [9]), and energy (e.g. methane production [4], and biofuels [10]. In many cases, expensive catalysts such as noble metals or extreme operating conditions traditionally required for these processes contribute significantly to the final cost. More active catalytic materials, that achieve higher throughput and better chemical control, provide an opportunity to produce more sustainable and affordable products.

Faster heterogeneous catalysts will require designing around the limiting constraints of surface chemistry and equilibrium. For example, the Sabatier principle quantifies the relationship between two or more slow elementary steps in a chemical surface reaction with transitions between rate-limiting phenomena occurring at maximum catalytic rate, as described by characteristic binding energies of the catalyst and adsorbents [11, 8, 12]. This trade-off is usually depicted through so-called volcano plots and implies the existence of an optimum catalyst best suited for each reaction when operating at static conditions [13]. In pursuit of improved catalysts, volcano plots have been identified for many important reactions including ammonia synthesis [14], oxygen evolution [15], and methanol synthesis [16]. Yet quantification of the rate limitations among different catalysts has so far not led to a new approach to catalyst design that experimentally exceeds the Sabatier limit.

One method to improve the performance of catalytic reactors introduces periodic behavior of controllable reactor parameters [17]. Dynamic (and specifically periodic) operation of catalytic reactors has already demonstrated enhancement of turnover frequency [17, 18] though various mechanisms including: oscillating feed concentrations [19], temperature [20], and partial/total pressure and flow [21, 22], or electrocatalytic potential [23, 24]. Composition modulation in particular has been extensively reviewed by Silveston [25]. With progressive advances in experimental methods, (specifically, precise control of the forcing schedule and real-time measurement of the response), computational modeling work could be validated against experimental data. Specifically it was shown [26, 27, 20] that periodically forcing a Pt catalyst through spatiotemporally varying heating protocols can lead to marked enhancement of the overall CO oxidation rate. In that case, the forcing was introduced through a localized temperature increase induced by a narrowly focused laser beam. Advances in experimental reactor technology (such as reverse flow reactors) continue to explore the expanded parameter space of periodic reactor operation through variable temperature, pressure, and composition [28, 22].

More recently, new synthetic capabilities have allowed for the controllable variation of the electronic state of catalysts themselves instead of reactor parameters [29]. These “programmable” catalysts can be continuously perturbed into new electronic states via predesigned “programs” that are optimized for cat-
alytic performance in selectivity and rate. Periodic catalyst perturbations can be applied directly via dynamical strain [30], light illumination that separates charge on the active site, [31, 32, 33], or by direct condensation of electrons or holes in a catalyst within a catalytic condenser [34]. These methods have demonstrated the ability to modulate the binding energy of molecules on surfaces by a significant fraction of an electron-volt, leading to new possibilities for oscillating the reactivity of molecules on surfaces as fast or faster than the static turnover frequency [35].

The motivation for oscillating the catalyst instead of the reactor or process derives from the speed of the oscillations possible in programmable catalysts that lead to transformational catalytic activity and selectivity control. For example, the surface of a catalytic condenser has been shown to oscillate as fast as 3000Hz, with faster speeds achievable with further device design [35]. At these high frequencies, simulations of simple chemistries have shown that oscillation of the catalyst state between two sides of a Sabatier volcano can achieve catalytic rates orders of magnitudes beyond the Sabatier peak [17]. Rate acceleration was observed across a broad range of catalytic chemistry scaling relationships and even in multi-step competing reactions, indicating broad capability for controlling reactions [1].

One of the key challenges remains to understand the relationship between designed programs of perturbation (e.g., charge, light, or strain) and the resulting catalytic performance. Programmable catalytic systems exhibit complex behavior as they expand in chemical reaction network size and mix of scaling relationships between reaction intermediates and transition states. For example, in a recent simulation of ammonia synthesis on a periodically strained ruthenium surface, the same periodic strain wave was shown to both promote and slow the formation of ammonia when applied at different frequencies (350Hz versus 5kHz) [30]. Rationalizing the complex behavior of programmable systems will occur through mathematical interrogation of the dynamic models that describe the changes and interactions of elementary reactions.

The mathematical and simulation tools required to understand programmable catalysts can be adopted from the methods developed in the past century to study periodic reactors. Periodically-operated reactors have been extensively studied by Horn [36] and Bailey [37], who introduced the mathematical methodology for understanding the relationships between periodic forcing and reactor performance. Tomita and Kai [19] explored the response of periodically forced chemical kinetics to different forcing parameters of the forcing (such as the amplitude and frequency) and constructed the relevant bifurcation diagrams. Kevrekidis et al. [38, 39, 40, 41] systematically explored the dynamics of periodically forced chemical reactors and constructed detailed bifurcation diagrams for representative cases of kinetics (autocatalytic reactions, Langmuir-Hinshelwood kinetics) and forcing parameters (concentration, temperature). These works deal with dynamical systems that exhibit autonomous oscillations even without forcing; yet the analysis and scientific computing algorithms used are of general applicability.

In this work, we present the scientific computing tools to efficiently calculate
the response of programmable catalysts to external periodic forcing. Using this, we systematically explore different forcing protocol parameters to understand their effect on catalyst response. This, in turn, allows us to understand how to optimally tune the many new degrees of freedom that arise when the forcing protocol is introduced (and, in the process, introduce the concept of Bayesian continuation). It also enables to locate and understand the functional shape of optimal forcing protocols. The research is presented with an initial description in terms of equations, parameters, and forcing mechanisms of programmable catalysis case studies of single and multi-step elementary reactions (Sec. 2). The results are presented as an illustrative model to rationalize the mechanistic underpinnings of improved average reaction rates and the fine-tuning of the forcing protocol (i.e., perturbation program) permitted by rapid screening of dynamic parameters (Sec. 3). Our computational algorithms are discussed throughout the results section as the need for them arises, and the relevant details can be found in the Supporting Information (Sec. A). Finally, we revisit a catalytic CO-oxidation model for which periodic rate optimization was previously experimentally observed as an illustrative example of the power of dynamic simulation tools [26, 27, 20].

2 Methods

2.1 Models and Methods

We consider three illustrative chemical reaction schemes (a unimolecular surface reaction; a set of two parallel surface reactions; and CO catalytic oxidation on Pt(110)); and three different reactor configurations (a constant gas pressure reactor; a Batch reactor; and a catalytic CSTR). The first two systems illustrate programmable catalysis with oscillating binding energies; they share this forcing mechanism. The last system illustrates programmable catalysis with oscillating surface temperature. Four of the nine possible combinations are considered in this manuscript (see Table 1). Two of these are presented in the main text and the rest, in more detail, in the Sec. A of the Supporting Information.

<table>
<thead>
<tr>
<th></th>
<th>Constant Gas Pressure</th>
<th>Batch Reactor</th>
<th>CSTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimolecular S.R.</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parallel S.R.</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>CO Oxidation</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Summary of system and reactor case studies presented in this manuscript.

2.1.1 Model Description - Constant pressure unimolecular surface reaction

We first consider a simplified 2-dimensional surface catalysis model, adapted and slightly modified from [17], assuming constant gas phase partial pressures
for all species. The resulting dynamical system consists, therefore, of two linear Ordinary Differential Equations (ODEs), describing the time evolution of the surface coverages of species A and B:

\[
\begin{align*}
\frac{d\theta_A}{dt} &= k_f_1 P_A \theta^* - (k_{r_1} + k_{f_2}) \theta_A + k_{r_2} \theta_B, \\
\frac{d\theta_B}{dt} &= k_{r_3} P_B \theta^* - (k_{f_3} + k_{r_2}) \theta_B + k_{f_2} \theta_A.
\end{align*}
\]

In equations 1 and 2, \( \theta^* \) (equal to \( 1 - \theta_A - \theta_B \)) denotes the fraction of empty sites, \( P_A \) is the (constant) partial pressure of A equal to 99 bar and \( P_B \) is the (constant) partial pressure of B equal to 1 bar. Let \( x \) equal to \((\theta_A, \theta_B)^T\) denote the state vector, \( k = (k_{f_1}, k_{f_2}, k_{f_3}, k_{r_1}, k_{r_2}, k_{r_3})^T \) the vector of kinetic parameters and \( \dot{x} = f_{\text{vf}}(x(t); t, k) \) the corresponding vectorfield described by Eqs. 1 and 2. Most kinetic parameters are a function of the relative binding energy of B, \( \Delta BE_B \), as described in [17]. We consider the case where oscillations in \( \Delta BE_B \) are enforced externally, so that the dynamical system becomes non-autonomous. Specifically, the value of \( \Delta BE_B \) will change according to a repeating step forcing function (see Fig. 1(A)). The step forcing function has four degrees of freedom (i.e., belongs to a four-dimensional parameter family of shapes). Here, we will choose the following parametrization:

- Forcing Frequency, \( f = \frac{1}{T} \),
- Duty cycle, \( \phi = \frac{\tau}{T} \),
- Amplitude, \( \Delta U = U_R - U_L \),
- Lower oscillation end-point, \( U_L \).

The analytical expression of the step forcing function then becomes:

\[
\Delta BE_B(t) = \begin{cases} 
U_R(\equiv U_L + \Delta U), & 0 \leq t \mod T < \phi T \\
U_L, & \phi T \leq t \mod T < T
\end{cases}
\]

Denoting \( p = (f, \phi, \Delta U, U_L)^T \) we can write \( \Delta BE_B = \Delta BE_B(p) \) or \( k = k(p) \). The non-autonomous dynamical system in Eqs. 1 and 2 is compactly denoted as \( \dot{x} = f_{\text{vf}}(x(t); t, p) \)

### 2.1.2 Model Description - Parallel Reaction Pathway in a CSTR

For a parallel reaction pathway chemical system, in a CSTR, the ODEs describing the time evolution of all species would be [18]:

\[
\begin{align*}
\frac{d\theta_A}{dt} &= k_f_1 P_A \theta^* - (k_{r_1} + k_{f_2}) \theta_A + k_{r_2} \theta_B, \\
\frac{d\theta_B}{dt} &= k_{r_3} P_B \theta^* - (k_{f_3} + k_{r_2}) \theta_B + k_{f_2} \theta_A.
\end{align*}
\]
\[
\frac{dC_A}{dt} = \frac{\dot{q}}{V}(C_A - C_{A,\text{feed}}) - k_1 \frac{N_{\text{sites}}}{V} \theta^* + k_2 \frac{N_{\text{sites}}}{V} \theta_A \tag{3}
\]
\[
\frac{dC_B}{dt} = \frac{\dot{q}}{V}(C_B - C_{B,\text{feed}}) - k_6 \frac{N_{\text{sites}}}{V} \theta^* + k_5 \frac{N_{\text{sites}}}{V} \theta_A \tag{4}
\]
\[
\frac{dC_C}{dt} = \frac{\dot{q}}{V}(C_C - C_{C,\text{feed}}) - k_{10} \frac{N_{\text{sites}}}{V} \theta^* + k_9 \frac{N_{\text{sites}}}{V} \theta_C \tag{5}
\]
\[
\frac{d\theta_A}{dt} = k_1 p_A \theta^* - (k_2 + k_3 + k_7) \theta_A + k_4 \theta_B + k_8 \theta_C \tag{6}
\]
\[
\frac{d\theta_B}{dt} = k_6 p_B \theta^* + k_3 \theta_A - (k_4 + k_5) \theta_B \tag{7}
\]
\[
\frac{d\theta_C}{dt} = k_{10} p_C \theta^* + k_7 \theta_A - (k_8 + k_9) \theta_C, \tag{8}
\]

where \(\dot{q}\) is the volumetric flow rate, \(C_{X,\text{feed}}\) is the feed concentration of species \(X\) and \(N_{\text{sites}}\) is the moles of the empty sites. More information about Eqs. 3-8 can be found in Section A.3 of the Supporting Information.

For the remaining chemical systems studied in this manuscript, the reader is directed to the Supporting Information (correspondence can be found in Table 2):

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unimolecular S.R.</td>
<td>Sec. 2.1.1 A.1</td>
</tr>
<tr>
<td>2</td>
<td>Parallel S.R.</td>
<td>Sec. 2.1.2 A.2 Sec. A.3</td>
</tr>
<tr>
<td>3</td>
<td>CO Oxidation</td>
<td>Sec. A.4</td>
</tr>
</tbody>
</table>

Table 2: References to the main text or Supporting Information with further details (equations, parameters) about each system/reactor configuration presented in this manuscript.

2.2 (Computational) Methods

2.2.1 The Stroboscopic map and its Fixed/Periodic Points.

One can discover periodic steady states\(^{1}\) by brute-force direct integration of the system’s ODEs, until convergence to a stable periodic oscillation (e.g. by tracking the state vector at a fixed phase, as in [1]). This approach only locates stable periodic solutions.

As an alternative to direct integration one can solve for the limit cycles as a boundary value problem in time with Newton’s method (Eq. B.7). Solving this boundary value problem via shooting (employing the variational equations

\(^{1}\)Here the term “periodic steady state” is used to denote a periodic solution of the forced problem (which clearly must have a period that is an integer multiple of the period of the forcing).
to evaluate the Jacobian of the Newton iteration) locates the limit cycles as fixed points of the stroboscopic map (see B.1). For linear systems (such as that described by Eqs. 1-2), this approach reduces to solving a system of linear equations.

Algorithms that parsimoniously integrate the variational and sensitivity equations in tandem with the system integration during shooting have been devised (see, for example, ODESSA and DASSL/DASSPK, [32]) and these days automatic differentiation can also be employed [43]. Algorithms alternative to (possibly multiple) shooting and associated software have also been in existence (e.g. AUTO, [44]). The monodromy matrix (the result of integrating the variational equations) quantifies the stability of the computed periodic solution, and the sensitivity vector (the result of integrating the sensitivity equations) facilitates its parametric exploration.

For problems with a large number of variables (e.g. for kinetic schemes with large numbers of intermediate species), even for just linear periodically forced problems, techniques of matrix-free, iterative linear algebra (like matrix-free Krylov methods, [45, 46]), that do not assemble the monodromy matrix for a linear solve, but are rather based on (a few) direct simulations from algorithmically selected sets of initial conditions, are available. They were historically developed at times (late 1970, early 1980) when CPUs had severe fast memory limitations.

2.2.2 High-dimensional mechanisms: Newton Krylov-GMRES

For nonlinear problems, like our non-constant gas phase pressure examples, or our CO oxidation example, solving the boundary value problem to locate the periodic solution via shooting requires an iterative procedure, like the Newton-Raphson (e.g. [38]).

When the number of unknowns becomes large, and the storage of the variational integration quantities becomes impractical, matrix-free algorithms (like Newton-Krylov-GMRES) allow us today to work with problems with very large numbers of state variables (e.g. combustion kinetic schemes with many active intermediates, or fine discretizations of reverse flow reactors/pressure swing adsorption beds).

Computationally locating periodic steady states as fixed points of the stroboscopic map can also be performed without full integration of the variational equations, through a matrix-free Newton-Krylov GMRES approach described in Sec. B.3. This implies that our computational toolkit can be also practically useful also for truly high-dimensional systems (i.e. complex kinetic schemes with massive numbers of intermediates and reactions between them) avoiding prohibitive memory requirements [47, 48]. An example of Newton-Krylov GMRES computation can be found in B.3 it is not necessary to resort to these techniques for the low-dimensional systems we work with here, but it is included for completeness.

Detailed information about the remaining algorithms of the toolkit, as well as more details about the ones already mentioned, can be found in the Support-
ing Information. For a summary, see Table 3:

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Algorithm</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed point approach for periodic steady states</td>
<td>Variational Equations</td>
<td>Sec. B.1</td>
</tr>
<tr>
<td></td>
<td>Augmented Stroboscopic Map</td>
<td>Sec. B.2</td>
</tr>
<tr>
<td></td>
<td>NK-GMRES</td>
<td>Sec. B.3</td>
</tr>
<tr>
<td>Optimizing</td>
<td>Bayesian Optimization</td>
<td>Sec. B.4</td>
</tr>
<tr>
<td></td>
<td>Bayesian Continuation</td>
<td>Sec. B.5</td>
</tr>
</tbody>
</table>

Table 3: Summary of algorithms used, along with corresponding references to the Supporting Information for further details.

3 Results & Discussion

3.1 Programmable Catalysis with Oscillating Binding Energies

3.1.1 Discovering periodic steady states

To contrast direct simulation with fixed point computation, we locate periodic steady states (with the same accuracy) initializing from the same initial state (unloaded catalytic surface) and track some relevant performance metrics. In the present section (and Sec. 3.1.2), the linear equation system described in Sec. 2.1.1 will be used. This is performed for three frequency values ($f = 10^2, 10^3, 10^4$ Hz), representative of an entire range of behaviors.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$t_{Newton}/t_{Integration}$</th>
<th>Integration Periods</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2$</td>
<td>1.32</td>
<td>21</td>
</tr>
<tr>
<td>$10^3$</td>
<td>0.20</td>
<td>266</td>
</tr>
<tr>
<td>$10^4$</td>
<td>0.03</td>
<td>2164</td>
</tr>
</tbody>
</table>

Table 4: Performance comparison between brute-force integration and Newton’s method (with the variational equation approach) for a linear system, for three different forcing frequencies. The remaining forcing parameters are fixed at $\phi = 0.5, U_L = -0.1eV, \Delta U = 0.6eV$. Corresponding trajectories can be found in Fig. B.9 at the Supporting Information.

Table 4 provides useful information both for algorithm performance and for the system’s transient dynamics. To begin with, all integration trajectories start with $(\theta_A, \theta^*) = (0, 1)$, i.e. with no adsorbates on the catalyst’s surface. The rate of simulation convergence to the periodic steady state strongly depends on the forcing frequency. For small frequencies (equivalently, large periods), such as $f = 10^2$ Hz, integration converges after a few periods. With increasing forcing frequencies (equivalently, smaller periods), the integration time required grows considerably (see Table 4). This can be understood in terms of the dynamics:
when each half forcing step lasts longer, the system has adequate time to move towards the respective steady state, before switching to the second half-step. This directly affects the time that brute-force integration takes to converge. In contrast, the time required for Newton’s single fixed point iteration is not greatly affected by the forcing frequency. Similar observations arise for nonlinear systems, where Newton’s method typically requires more than one iteration for convergence. Again, we search for periodic steady states (with the same accuracy) initializing from the same initial state as direct simulation. Here, the equation system described in Sections 2.1.2 of the main text and A.3 of the Supporting Information will be used (with, however, fixed volumetric flow rate). The computations are performed for three representative frequency values ($f = 5, 100, 10000$Hz).

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$t_{\text{Newton}}/t_{\text{Integration}}$</th>
<th>Integration Periods</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.11</td>
<td>50</td>
</tr>
<tr>
<td>100</td>
<td>0.17</td>
<td>558</td>
</tr>
<tr>
<td>1000</td>
<td>0.03</td>
<td>1732</td>
</tr>
</tbody>
</table>

Table 5: Performance comparison between brute-force integration and Newton’s method (with the variational equation approach) for three different forcing frequencies. Corresponding trajectories can be found in Fig. B.10 at the Supporting Information.

Newton’s method can, and will (with a good initial guess) be much more efficient, especially for larger frequencies (taking, for example no more than 4% of the time compared to brute-force integration, as shown in Tables 4 and 5). It is also important to note that brute-force integration can locate only stable periodic steady states, while Newton’s method (depending on initialization) can also locate unstable steady states. This makes Newton’s method also suitable for stability and/or bifurcation analysis in systems with multiple coexisting solutions, a phenomenon frequently observed in catalytic ignition.

### 3.1.2 Rationalizing improved performance under periodic forcing

The dynamics of the mechanism described in Sec. 2.1.1 consist of six elementary processes: Adsorption of A, Desorption of A, Forward and Reverse surface reaction, Adsorption of B, and Desorption of B. Adsorption of both species does not require activation, in contrast to the rest of the processes.

As can be seen from Fig. 1(B), during stage R, the surface reaction energy barrier is reduced, and the desorption of B energy barrier is increased. This stage therefore favors the surface reaction. Conversely, stage L favors the desorption of B, and the surface reaction rate is reduced. In other words, stage R induces a bottleneck in the desorption of B, while during stage L the bottleneck is shifted to the surface reaction.

The limiting process of each forced oscillation stage is directly reflected on the surface coverages of the chemical adsorbates (here, we choose to study the surface coverage of A and the surface coverage of empty sites - Fig. 1(C)). During
Figure 1: Oscillation of the binding energies between stages R and L lead to oscillations of all chemical species (and functions thereof): (A) Step forcing function, (B) Energy diagram of the two stages of the step forcing function. The stage colored red ($U_R$) favors the surface reaction step, while the blue colored stage ($U_L$) favors desorption, (C) Four oscillations of two of the system variables: $\theta_A$, the surface coverage of $A$, and $\theta^*$, the surface coverage of empty sites. Blue and red colors denote the oscillation stage (see panel (B)), (D) A phase portrait point of view of the oscillations. The points of stage change are denoted on the limit cycle. (E) Static steady states and their slow and fast eigendirections are shown on the limit cycle figure. (F) The net desorption rate of $B$ of a number of points along the limit cycle. These points are separated by a fixed time step. Note that all these results are obtained for forcing parameters: $f = 10^3\text{Hz}$, $\phi = 0.5$, $U_L = -0.1\text{eV}$, $\Delta U = 0.6\text{eV}$. 

\[ \Delta U \]
stage R (red) limited desorption restricts the number of empty sites on the catalyst (low $\theta^*$), while the A adsorbates are reacting to B adsorbates. During stage L (blue) desorption is no longer limiting, and empty surface sites appear. At the same time, the now difficult surface reaction causes accumulation of A adsorbates (Fig. 1(C)). The phase portrait point of view is helpful, as it removes the time dependence and makes it easier to illustrate periodic steady states (Fig. 1(C)).

To rationalize the improvement in overall averaged reaction rate, it is useful to consider the steady state conditions at constant operating parameters corresponding to stages R and L. With slight abuse of nomenclature, we will call these “static steady states” (in contrast to the “periodic steady states” above). As seen in Fig. 1(E)&(F), the static steady states for each Programmable Catalysis stage provide very useful information about the forced limit cycle. This forced limit cycle “visits” intermediate surface coverages compared to the two static steady states. Each of these static steady states decidedly favors one of the two adsorbates (A or B), as the limiting step is different at the conditions of each of them. The composition at these states is shown in Table 6.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$(\theta_A, \theta^*)$ Coordinates</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>(0.0132, 1.35 $\cdot$ $10^{-13}$)</td>
<td>$(-10^8, -81.9)$</td>
</tr>
<tr>
<td>L</td>
<td>(9.994, 1.23 $\cdot$ $10^{-9}$)</td>
<td>$(-10^8, -194.8)$</td>
</tr>
</tbody>
</table>

Table 6: Static steady states for each forcing stage and their eigenvalues.

The eigenvalues of the Jacobian of our linear problem at each of the static steady states (Table 6) confirm that both of them are stable, and reveal a significant separation in timescales for each one of them. Knowing the eigendirections of the respective linearization eigenvectors, we know the slow and fast linear subspaces for each of the steady states. These subspaces inform us about the slow and fast directions along the limit cycle itself (see Fig. 1(E)). This is confirmed by the density of (equally spaced in computational time) points on the limit cycle (Fig. 1(F)): The vast majority of points can be found where the limit cycle is moving along slow eigenvectors, and towards corresponding static steady states.

Fig. 1(F) associates different parts of the limit cycle with the net desorption rate of B. The net desorption rate of B is significantly greater during stage L. This fits with the qualitative understanding we already have: Stage L promotes desorption of B, by decreasing the energy barrier required for it. However, the closer we move to the static steady state, the lesser the net desorption rate of B. This can be clearly seen in the Fig. 2 where the same system is presented in 3D. As a metric for each forcing parameter configuration, we will use the period-averaged net desorption rate of B, defined as:

$$NDR_B = \frac{1}{T} \int_0^T NDR_B(t) dt.$$

(9)
Figure 2: 3D view of the periodically forced limit cycle \( f = 10^2 \text{Hz}, \phi = 0.5, U_L = -0.1 \text{eV}, \Delta U = 0.6 \text{eV} \) where the instantaneous Net Desorption rate of B is now the \( z \)-axis. Static Steady states are denoted as stars (red for stage R and blue for L). The corresponding slow eigendirections are colored green and the fast ones, orange. Direction arrows on different parts of the limit cycle are colored analogously. The projection of the limit cycle is seen on the “floor” of the 3D plot - compare with Fig. 1(E-F).

It is interesting to notice in Fig. 2 that both the static steady states have a very low net desorption rate of B. This can be explained by the fact that the dynamics of each static system are fully constrained by the respective limiting process (desorption or reaction). This observation further corroborates the benefits of Programmable Catalysis, by juxtaposing static and dynamic performance for each stage.
Different Programs. We will now explore the effect of a few periodic forcing parameters on the behavior at different stages and on the overall performance.

First we explore the effect of the forcing frequency on the dynamics. Fig. 3(A) shows the effect of extreme values of the forcing frequency. For very low frequencies (left panel in Fig. 3(A)), the system has enough time to approach the respective static steady state of each stage. As a result, the system spends considerable time on the slow eigendirections, especially close to the static steady states (where the dynamics get exponentially slow). Even if the system instantaneously reaches higher net desorption rates of B, it spends considerably more time in less productive states and, therefore, the result is a lower period-averaged net desorption rate of B ($NDR_B = 23.2s^{-1}$). The characteristic times of the slow eigendirections confirm this conclusion ($2f < \lambda_{L,slow}, 2f < \lambda_{R,slow}$).

In the case of very fast frequencies (right panel in Fig. 3(A)) the extremely short oscillation periods do not allow the system to reach/be affected by the slow eigendirections. In fact, the oscillation periods are even shorter than the fast characteristic times of either of the two static steady states ($2f > \lambda_{L,fast}, 2f > \lambda_{R,fast}$). Even the fast stable eigendirections are not visited by the trajectory. The period-averaged net desorption rate of B does not appear sensitive to the frequency at such high frequencies ($NDR_B = 27.7s^{-1}$); compare to that of the middle panel of Fig. 3(A) ($NDR_B = 27.7s^{-1}$).
Fig. 3(B) shows the effect of changing the duty cycle \( \phi \) while keeping all the other forcing parameters fixed. In the case where stage R lasts longer (right panel in Fig. 3(B)) the limit cycle becomes located closer to the static steady state of stage R (where the dynamics are slower). Necessarily, during stage L, the limit cycle lies further away from the static steady state of stage L, which causes a higher net desorption rate of B. However, this highly productive state doesn’t last long, and the performance is, on average, worse \( (\overline{NDR}_B = 26.0 \text{s}^{-1}) \) than the case of equally lasting stages \( (\overline{NDR}_B = 27.7 \text{s}^{-1}) \).

In contrast, in the case when the L stage lasts longer (left panel of Fig. 3(B)), the opposite effect is observed: the limit cycle approaches the static steady state of stage L but now neither stage is productive enough to make a difference \( (\overline{NDR}_B = 17.3 \text{s}^{-1}) \).

In general, when changing the duty cycle \( \phi \) a very interesting trade-off arises: more productive states (such as those in the right panel of Fig. 3(B)) can be only reached for a shorter time duration, so that the system always keeps a “safe distance” from the L static steady state. This behavior suggests the existence of an optimum w.r.t. the duty cycle.

Similar computational examples can be performed to study the effects of the amplitude \( \Delta U \) and the lower oscillation endpoint \( (U_L) \). Note that when comparing such cases, the static steady states, their eigenvalues and stable eigendirections will be different for every forcing parameter value.

### 3.1.3 Continuation

Pseudo-arclength continuation \([49, 50, 51]\), allows the efficient exploration of responses along a broad parameter range. Here, we employ the commercial software AUTO 07p \([44]\) to explore how a batch reactor with a parallel reaction pathway responds to a range of forcing frequencies (details about model and results in \(A.2\)).

In accordance to the analysis in Sec. 3.1.2 a strong dependence of the resulting dynamics on the forcing frequency can be observed. At very low frequencies (or high periods) the batch reactor system has adequate time to move towards the static steady states and the catalytic surface ends up being covered with either one of the two adsorbed products at each stage. On the contrary, when the oscillations are too fast, the surface coverages do not have time to vary much, and, in fact, the surface is covered with the species most difficult to desorb “on average” (i.e. species C).

Next, we perform continuation for a CSTR with a parallel reaction pathway (model described in \(A.3\)). In the case of a CSTR, turnover frequencies can be used to quantify performance

\[
TOF_X(p) = \frac{\dot{q}}{TN_{sites}} \int_0^T C_X(t; p) \, dt,
\]

for any species X. In Eq. 3.1.3 \( p \) is the forcing parameter vector, \( \dot{q} \) is the volumetric flow rate of the CSTR, \( T \) is the forcing period (= 1/f, component
of \( p \), \( N_{\text{sites}} \) is the number of empty catalytic sites and \( C_X \) is the concentration of \( X \), a component of the state vector.

With the results of Ardagh et al. [18] as a starting point, we explore how the turnover frequency of \( A \) (\( \text{TOF}_A \)) changes w.r.t. two forcing parameters. Although the duty cycle was not considered in [18], here we show that tuning it can further improve \( \text{TOF}_A \). To show this, we select the best performing \( U_L \) from Fig. 3 in [18] (i.e. \( U_L = -1.46 \text{eV} \)), choose the same fixed amplitude \( \Delta U = 0.6 \text{eV} \) and vary the frequency \( f \) and duty cycle \( \phi \). To approximate the \( \text{TOF}_A \) surface, a “scaffolding” is constructed by evaluating the quantity on a regular grid in the \((\log_{10} f - \phi)\) parameter space.

![Figure 4](image)

**Figure 4:** (A) Two parameter solution surface approximated by a grid of points where periodic steady states are found using Newton’s method (here, reporting the turnover frequency of \( A \) for each such state). Red line corresponds to the zoomed region on the right upper inset. All calculations were performed for fixed \( U_L = -1.46 \text{eV}, \Delta U = 0.6 \text{eV} \). (B) Optimization result overlayed on the one-parameter continuation branch (for comparison, see right upper inset of (A)). The Bayesian Optimization optimum location is consistent with the continuation computations. (C) Optimal forcing function shape.

As can be seen in Fig. 4(A) the CSTR performs better at higher forcing frequencies, something that is confirmed in Fig. 3 of [18]. We posit that this
is associated to the characteristic times of the two static steady states, as we explained in Sec. 3.1.2. There is an optimum with respect to the duty cycle, which we hypothesize is attributed to a trade-off similar to the one presented in Fig. 3(B). As a result, we achieve a slightly better maximum turnover frequency of 107.4s⁻¹ compared to the one found in [18], i.e. 101s⁻¹.

3.1.4 (Bayesian) Optimization

After rationalizing Programmable Catalysis by relating it to the static steady state properties and the transitions between them, finding solutions efficiently and continuing them, the next natural step is to focus on optimization. Specifically, we will deal with maximizing the turnover frequency of A (TOFₐ). The optimization problem can be formulated as:

\[ p^* = \arg \max_p \{ TOF_A(p) \} \]  

(11)

We will first validate our approach against the results in Fig. 4(A) using the Bayesian Optimization (BO) and Continuation (BC) framework discussed in the Supporting Information (Sections B.4 and B.5). We opted for Bayesian Optimization (BO) because the optimization problem at hand is expensive, black-box and with no known derivatives [52]. Bayesian Continuation (first introduced here) alleviates the high function evaluation cost for every BO iteration, resulting in considerable overall acceleration. For validation purposes, a one-parameter continuation is performed w.r.t. \( \phi \) for \( \log_{10} f = 4 \) (the solution branch corresponding to the right-top panel of Fig. 4(A)).

Fig. 4(B) validates the BO framework: the optimum indeed coincides with the one found by detailed continuation results (specifically, \( p = (\log_{10} f^*, \phi^*) = (4, 0.787) \), see Fig. 4(C) for the corresponding forcing function shape). After finding the optimal forcing parameters, we will utilize insights from Sec. 3.1.2 to understand how this optimum arises.
Figure 5: The forced limit cycle corresponding to the optimal forcing function shape found with Bayesian Optimization (Fig. [B.4]). Also plotted, are the two static steady states and all relevant eigendirections/ stable (sub)manifolds. The black arrows on the limit cycle denote the direction of time. Further information can be found in Fig. [B.12] of the Supporting Information.

As can be seen in Fig. 5 the eigendirections of the static steady states again provide useful information about the dynamics of the forced limit cycle. As expected from the analysis in Section 3.1.2 the limit cycle spends a long time on the slow (sub)manifolds at each stage. However, in this case, there are multiple slow eigendirections, corresponding to multiple timescales. Furthermore, the (sub)manifolds are nonlinear curves and the forced limit cycle high-dimensional, rendering visualization difficult: we have to rely on the qualitative study of projections. Interestingly, the interplay of many different slow timescales can be observed on the limit cycle, such as the one here for stage L. The respective eigenvalues can inform us about the relation between the characteristic times of each slow eigendirection and how each relates to the forcing period (see left panel of Fig. [B.12] in the Supporting Information). As expected, the important slow (sub)manifolds have characteristic times comparable to those of the imposed forcing.
As discussed in Sec. 3.1.2, an optimum w.r.t. \(\phi\) can arise as the result of a trade-off between parts of the oscillation spent in the different stages: staying longer or shorter in the reaction promoting stage R results in lower final \(TOF_A\); and the overall average rate will therefore be less. One can examine the time series of \(TOF_A\) for various \(\phi\) values to confirm this (see right panel of Fig. B.12 in the Supporting Information).

So far, we have optimized the shape of the forcing function, within an (at most) 4-dimensional family of step functions. It is possible to further vary the forcing policy shape, and thus add degrees of freedom to the optimization, at the cost of increasing overall complexity; this is done by considering a versatile set of basis functions that can parametrize many shapes, for example, Radial Basis Functions (RBFs) [53].

In the context of Programmable Catalysis, the relative binding energy of A can be expressed, using \(N\) RBFs, as:

\[
\Delta BE_A(t) = w_0 + \sum_{i=1}^{N} w_{\text{amp}_i} e^{w_{\text{spread}_i}(t-w_{\text{center}_i})^2}.
\]

This would result in \(3N + 1\) - dimensional family of shapes for \(N\) RBFs. Denoting \(w = [w_0, w_{\text{amp}_1}, \ldots, w_{\text{amp}_N}, w_{\text{center}_1}, \ldots, w_{\text{center}_N}, w_{\text{spread}_1}, \ldots, w_{\text{spread}_N}]\) the optimization problem now becomes:

\[
\mathbf{w}^* = \text{argmax}_{\mathbf{w}} \{TOF_A(\mathbf{w})\}.
\]

To establish the benefits of expressing forcing shapes with more RBFs, we will attempt to further improve the optimum step forcing function shape found with Bayesian Optimization (Fig. 4(C)) by adding a single radial basis function on the L stage and optimizing its shape.

This can be imposed by restricting \(w_{\text{center}}\) in \([\phi^*, 1]\), where \(\phi^* = 0.788\) as found in Fig. 4(B). Note that the rest of the step function shape parameters are kept fixed: \(f = 10^4\text{Hz}, \Delta U = 0.6eV, U_L = -1.46eV\). To keep upper and lower bounds the same, we fix \(w_0 = 0\) and truncate any RBF at \(U_R = U_L + \Delta U\). As for the amplitude of the RBF \(w_{\text{amp}}\), we arbitrarily bound it in \([0, 2]\) and the spread \(w_{\text{spread}}\) at \([10, 10^4]\). These bounding choices are arbitrary, yet reasonable, and cause no loss of generality for our computations: too high values of \(w_{\text{amp}}\) seem to have little effect on the shape of Eq. 12 because of the truncation, and too high values of \(w_{\text{spread}}\) create too large potential gradients.

The optimum found is \(TOF_A(\mathbf{w}^*) = 112.5s^{-1}, \mathbf{w}^* = [0, 2, 0.866, 3.76]\). In this case, the addition of one RBF to forcing has led to further improvement of the performance of the catalytic reactor. It is, we believe, remarkable to analyze in detail how this new improvement arises.

We argue that it is not simply the result of extension of the “residence” of the dynamics in one of the two stages, but rather the result of a new optimal dynamic oscillation shape. Indeed, if we use a single step forcing with duty cycle equal to the sum of first stage durations of our optimal forcing function (\(\phi = 0.787 + 0.022\)), the performance is worse \((TOF_A = 107.39s^{-1})\).
Optimal forcing protocols guide the dynamics of the system to most productive states by exploiting the differences in the characteristic times of the static steady states. To illustrate this, we plot a projection of the forced limit cycles of (a) the optimal step forcing as well as (b) the optimal “step plus one RBF” forcing, and turn to the eigendirection analysis for insights.

Figure 6: Forced limit cycle projections for the two optimal solutions found: one for the optimal single step forcing function (blue) and one for the optimal “step plus one RBF” one (red). The upper left insets show these two optimal forcing functions. The right inset shows a zoomed region where the trajectories of the two forced limit cycles diverge, along with the relevant static steady state slow eigendirections. Note that the steady states (and respective eigenvalues/ eigenvectors) will be slightly different for the two cases shown here; we include one of the two sets, for simplicity.

As expected and confirmed by Fig. 6, these two cases have similar dynamics most of the time, i.e. the respective limit cycles move mostly along (and jump
across) the same slow eigendirections. In the case of the “step plus one RBF” (colored red), the second forced limit cycle solution suddenly diverges from the first (around point B) and follows a different trajectory, with a new, added loop, leading back to the slow eigendirection of stage R (coinciding with the plateau between points B and C at the top left inset of Fig. 6). After a while, the trajectory returns again close to the point of initial divergence, and rejoins the first optimal trajectory (colored blue)(points A,C). The single step optimal trajectory ends up spending time at a much slower, and reactively unproductive, eigendirection (deep black in the inset). The “step plus one RBF” optimal trajectory gets “kicked off the course” of the first by the additional RBF, as seen in the inset of Fig. 6. In other words, the optimal additional RBF prevents the limit cycle from spending useful time in an unproductive state, and kicks it back to a productive one. This observation further corroborates the argument that it is the shape of the forcing function that matters, as it can be selected to optimally assist the system dynamics to spend time along more productive states (more productive static steady state slow eigenvectors).

The next step is to completely rely on RBFs for the construction of useful forcing function shapes. To demonstrate this, we formulate a new optimization problem similar to Eq. 13 with the superposition of two radial basis functions. We choose to keep $w_0$ fixed at $-1.46\text{eV}$, and also $f = 10^4\text{Hz}$. The chosen value of the fixed frequency is based on our knowledge of the characteristic times. We also choose to keep the rest of the constraints used in the optimization of one RBF, with the exception of the $w_{\text{center}}$ parameter: we contain the first RBF on the first 60% of the period and the second at the last 60%. This constraint allows for some overlap of the RBFs but avoids problematic RBF permutations. The resulting optimization problem is over a 6-dimensional family of shapes.

In this case, BO converges to “familiar” shapes: some optima resemble the optimal single step forcing function shape in Fig. 4(C), while some the “single step plus added RBF” shape in Fig. B.14. This similarity is reflected on similar values of $TOF_A$. The above observation demonstrates how RBFs can be used as a universal approximator for shapes, and can thus be superimposed to construct forcing functions of any complexity.

3.2 A non-linear example: CO-Oxidation

We now revisit a more realistic example: CO-oxidation on Pt(110) at very low pressures. This example has been experimentally studied in the literature (in collaboration with the FHI group of Prof. G. Ertl in Berlin [26, 27]; here, the periodic forcing of the local temperature on the catalyst crystal was realized through using a focused laser beam periodically scanning a circular path of $L = 4.48\text{mm}$ perimeter. This example allows to extend the linear modeling considerations above to nonlinear systems (slow nullclines -the quasi-steady states of fast reactions- will now take on the role of slow eigenvectors). Surprisingly, it also allows to visualize the mechanisms underpinning dynamic operation rate improvement. When the focused laser beam periodically scans (with constant speed $v$) the aforementioned circular path at a specific speed, we can realisti-
cally assume that it induces, at every point along the path the same oscillatory temperature profile but at a different phase! Those researchers were thus able to simultaneously visualize (using PEEM, Photo-Emission Electron Microscopy) in a single snapshot all phases of the periodically forced system response. A simulation of this configuration (along with the resulting catalytic reaction rate) can be computed using the Krischer-Eiswirth-Ertl \cite{54} system of Eqs. A.18-A.20 (reported in the Supporting Information).

\( \text{CO}_2 \) production rate was maximized as a function of the laser scanning speed (corresponding to the frequency of the forcing) computationally for this configuration in \cite{20} -and experimentally, for a slightly different spatiotemporal forcing configuration in \cite{55}. In particular, starting from a condition where the Pt surface is covered by adsorbed CO (leading to low \( \text{CO}_2 \) production rate), local laser-excitation converts the surface to an excitable state and accelerates CO desorption. Depending on the scanning speed (i.e. the characteristic time required for the surface to return after excitation to its quenched temperature) one can observe different \( \text{CO}_2 \) production rates, with maximum values attained at a specific laser beam traveling speed (specific temperature forcing frequency). Indeed, the darker arc of the experimental snapshot in Fig. 7(F) shows that, during that portion of the forcing cycle, oxygen adsorbs dissociatively on the surface, so that the reaction can actually proceed.

We performed a systematic computational exploration optimality w.r.t laser speed using our algorithmic toolkit (see Supporting Information, Sec. B); we found a characteristic laser speed that maximally enhances \( \text{CO}_2 \) production (see Fig. 7(B)).

Figs 7(C)&(D) are a nonlinear analog of the optimal forcing linear phase portrait plots in Figs 2 & 5. What was a “slow eigenvector” for linear problems now becomes a “slow nullcline” (i.e. the nullcline corresponding to a slow variable) for the nonlinear problem. As is shown in the Supporting Information (Fig. A.8), slow (fast) eigenvectors of the linearization at one of the steady states involved are tangent to the corresponding slow (fast) nullclines.
Figure 7: (A) Top panel: Periodic temporal variation pattern of the substrate temperature at a specific point of the Pt catalyst. Experimentally, the temperature variation was induced by a laser spot which scans a path on the Pt catalyst with period, $T_{\text{force}} = 80s$. (A) Bottom panel: Evolution of CO (black dash-dot line), O (black solid line) surface coverage (left axis) and CO$_2$ production rate (red line, right axis) during the first 200s of laser scanning. Periodic variation of the temperature induces a corresponding periodic variation of the surface coverages and the production rate. (B): Dependence of CO$_2$ production rate enhancement on the frequency of the periodic forcing (i.e. the speed of the laser spot scanning a circular path). The solid lines correspond to period-1 solutions, and the red dots represent turning point (saddle-node) bifurcations. The orange bordered rectangle includes period-2, 3, 4, ... forced periodic solutions. (C) & (D): Phase portraits ($T_{\text{forcing}}$ lines) for the optimal laser forcing speed, $v = 96.9 \mu m/s$ (blue line). Red and black solid lines depict the $\frac{\partial \theta_{CO}}{\partial t} = 0$, nullclines for temperatures, 541K and 544K, respectively. Red and black dashed solid lines represent the $\frac{\partial \theta_{1,k+1}}{\partial t} = 0$, nullclines for temperatures, 541K and 544K, respectively. The green star is added for easier orientation. The right panel illustrates the $\theta_{CO}$-$\theta_{1,k+1}$ plane projection of the left panel 3D figures. (E) & (F): Periodically forced CO oxidation on a Pt catalyst: Qualitative comparison of our simulation results (left) versus results observed in the laboratory reproduced from [20] (right). Note that even though our computational model does not include dependence on physical space, we plot our (temporal) results on a circular disc, for qualitative correspondence with the experimental results.
4 Outlook: Application of Bayesian Optimization to Surface Chemistry

In future work, we plan to explore efficient optimization using more complex forcing function shapes within more complex chemical mechanisms. For surface chemistries such as ammonia or methanol synthesis, reactions occur on multiple sites (e.g., terrace, step, corner), and the molecules can decompose or form through different reaction pathways. This complexity increases the probability that optimal applied programs will be more complex than simple square waves. As the dimensionality of the optimization problem increases, we hypothesize that reduced Bayesian Optimization can significantly accelerate convergence [56]. We also intend to employ Global optimization approaches for Gaussian Processes used in Bayesian Continuation and Optimization [57].

5 Conclusions

Programmable catalysis has the potential to significantly improve the performance of catalytic reactors, and to facilitate the transition towards efficient and sustainable production of valuable chemicals. In this work, we evaluated case studies in recent literature to obtain deeper insights into the mechanisms of programmable catalysis and the features of the kinetics that are important when tuning the degrees of freedom corresponding to the forcing protocol (i.e., the program). Combining modern numerical methods with modern active learning schemes (in this case, Bayesian Optimization and Bayesian Continuation), we demonstrated efficient computational location of solutions, continuation of such solutions, and performance optimization. The data-driven nature of BO makes it also practically usable in the laboratory. The technical capability of generating forcing functions with a wide range of characteristic time scales lies at the heart of optimizing complex temporally multiscale reaction kinetic schemes. The ability to systematically design the interaction between the multiple intrinsic kinetic time scales and the (now practically realizable multiple forcing time scales underpins the remarkable promise of programmable catalysis.

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