

A Roadmap for Simulating Chemical Dynamics on a Parametrically Driven Bosonic Quantum Device

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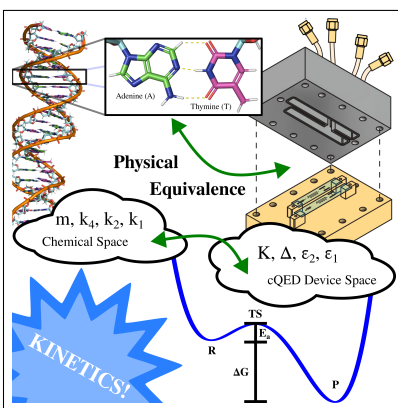
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Abstract

Chemical reactions are commonly described by the reactive flux transferring population from reactants to products across a double-well free energy barrier. Dynamics often involves barrier recrossing and quantum effects like tunneling, zero-point energy motion and interference, which traditional rate theories, such as transition-state theory, do not consider. In this study, we investigate the feasibility of simulating reaction dynamics using a parametrically driven bosonic superconducting Kerr-cat device. This approach provides control over parameters defining the double-well free energy profile, as well as external factors like temperature and the coupling strength between the reaction coordinate and the thermal bath of non-reactive degrees of freedom. We demonstrate the effectiveness of this protocol by showing that the dynamics of proton transfer reactions in prototypical benchmark model systems, such as hydrogen bonded dimers of malonaldehyde and DNA base pairs, could be accurately simulated on currently accessible Kerr-cat devices.

TOC Graphic



Computational modeling of reaction dynamics offers insights into the time scales and mechanisms of molecular transformations in chemical reactions, revealing the factors that determine the reaction rates and efficiencies. Most chemical reactions are multi-step processes, with each step described by the reactive flux transferring across a barrier of a double-well potential energy surface along the reaction coordinate. However, simulating these elementary steps can be challenging, especially when barrier recrossing and significant quantum effects are involved, such as tunneling, zero-point energy, and interference. These factors lead to a complex interplay between coherence and dissipative dynamics, which are not accounted for by traditional rate theories, such as transition-state theory.¹⁻⁶

Recent advances in quantum engineering have generated interest in developing quantum devices to simulate the quantum dynamics of atoms, molecules and condensed phase systems.^{7,8} Such analog quantum simulators can offer significant hardware efficiency advantage over general-purpose quantum computers, especially when the device Hamiltonian can be efficiently mapped onto the molecular system of interest. In this study, we explore the feasibility of using a Superconducting Nonlinear Asymmetric Inductive eLement (SNAIL) transmon⁹ to simulate quantum dynamics of elementary chemical reactions. The SNAIL device develops a double-well structure when operated under a continuous drive with frequency close to twice the SNAIL transmon resonance. This system is experimentally realizable in a superconducting quantum circuit and is referred to as Kerr-cat device.¹⁰ Its controllable parameters can be adjusted to model the asymmetric double-well free energy profiles of various molecular systems across a wide range of external conditions, including temperature and coupling strength between the system and the thermal bath of non-reactive degrees of freedom. Here, we explore the capabilities of SNAIL devices by simulating the chemical dynamics of prototypical proton transfer reactions in hydrogen-bonded complexes, using the SNAIL Hamiltonian parametrized for malonaldehyde dimers and DNA base pairs, as could be experimentally implemented today on currently available platforms. These simulations are currently unattainable with noisy intermediate-scale quantum (NISQ) computers, includ-

ing state-of-the-art conventional superconducting quantum computers, due to their circuit depth limitations. In contrast, we show that the SNAIL device could accurately capture the dynamics of these chemical reactions, effectively accounting for the delicate interplay between tunneling, zero-point energy, resonance, interference, and dissipative effects.

In transition-state theory (TST),¹⁻³ the reaction rate constant is given by the Eyring-Polanyi equation: $k_{TST} = \frac{k_B T}{h} e^{-\Delta G^\ddagger/k_B T}$. Here, ΔG^\ddagger is the Gibbs free energy of activation (the barrier height as measured from the minimum of the reactant well to the transition state configuration that corresponds to the barrier top), k_B is the Boltzmann constant, T is the absolute temperature, and h is the Plank constant. The Gibbs free energy of activation can be divided into enthalpy and entropy contributions: $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, where ΔH^\ddagger is the activation enthalpy and ΔS^\ddagger is the activation entropy. Identifying ΔH^\ddagger as the activation energy (E_a), the TST rate constant can be expressed by Arrhenius' law, $k_{TST} = A e^{-E_a/k_B T}$, with $A = \frac{k_B T}{h} e^{\Delta S^\ddagger/k_B}$ the rate constant for the barrierless case (i.e., when $\Delta H^\ddagger = E_a = 0$).

Deviations from TST and the Arrhenius law occur when the assumptions of these theories become invalid.^{11,12} Recrossing events and quantum phenomena like tunneling, quantum interference, and zero-point energy effects can lead to deviations from TST by introducing reactive pathways beyond classical barrier crossing.¹³ Some of those deviations can be approximately accounted for by the transmission coefficient κ , modifying the reaction rate constant to $k = \kappa k_{TST}$. This approach assumes that the reaction dynamics follows rate kinetics with a single well-defined rate constant. Another breakdown of TST occurs when the concept of a rate constant becomes invalid, such as when the barrier height is comparable to $k_B T$ or when the coupling between the reaction coordinate and other non-reactive molecular degrees of freedom (DOF) is weak.¹⁴ These forms of TST breakdown often stem from the inherently quantum-mechanical nature of chemical dynamics.¹⁵⁻¹⁷

A prime example of an elementary chemical reaction of fundamental biological importance, which is often modeled using a double-well potential energy surface, is the adenine-thymine proton transfer reaction in DNA.¹⁸⁻²⁰ The free energy profile for this reaction varies

with physiological conditions. Under normal cell conditions, the profile favors the hydrogen-bonded adenine-thymine complex form. However, during cell replication, this hydrogen bond must be broken to allow the DNA strands to duplicate. Proton transfer during this process has been suggested to cause spontaneous mutations due to bases occasionally adopting less likely tautomeric forms.²¹ Therefore, simulating the dynamics of proton transfer in the adenine-thymine complex across a broad range of double-well free energy profiles can provide insights into the potential influence of quantum effects on the interconversion between tautomeric forms of the bases.

The traditional method for testing and validating chemical rate theories, including both TST/Arrhenius and post-TST/non-Arrhenius approaches, has relied on extensive experimental measurements of chemical dynamics across a diverse range of molecular systems and external conditions to cover both chemical space and parameters influencing chemical dynamics, such as temperature and the interactions between the reaction coordinate and the non-reactive DOF. However, this approach is highly challenging and labor-intensive. This is because experimentally monitoring reactant and product populations in real time may prove difficult, and changing from one chemical system to another often involves altering multiple parameters with complex and sometimes opposite effects. A notable example of the difficulty of this traditional approach is the 30-year delay between the theoretical prediction of the inverted region in the Marcus rate theory for electron transfer reactions and its experimental validation.²²⁻²⁴

A promising alternative for experimentally testing and validating chemical rate theories has emerged with the advent of controllable and highly tunable fully quantum-mechanical platforms. These platforms can allow the exploration of quantum dynamics in various complex model systems across a broad range of parameter space.^{7,8,25} Considering that chemical dynamics is inherently quantum mechanical in nature and that the most under-explored regimes of chemical dynamics exhibit significant quantum effects, these platforms can offer valuable simulation tools to investigate chemical reactivity under conditions that could be

challenging for spectroscopic methods applied to molecular systems.⁷

Recent studies that exemplify this innovative approach of using quantum devices to explore chemical reactivity include the use of an ion trap platform as an analog simulator of the chemical dynamics underlying redox electron transfer reactions.^{26,27} Marcus theory, which describes the electron transfer rate constant with a double-well model, is analogous to TST for non-redox chemical reactions. It employs a TST-like argument with an Arrhenius-type expression for the rate constant.³ In Marcus theory, the transition state is the molecular configuration at the crossing point between the diabatic free energy profiles of the donor (reactant) and acceptor (product) states along the reaction coordinate associated with the reorganization of the nuclear DOF upon electron transfer. Like TST, Marcus theory treats the activation to the transition state as a classical process and assumes weak electronic coupling between the donor and acceptor states. Schlawin et al. demonstrated that an ion-trap device could reproduce the predictions of Marcus theory, including the inverted regime.²⁶ They also showed how this device could explore deviations from Marcus theory because of quantum (low-temperature) and strong electronic coupling effects. This enables the study of unconventional electron transfer regimes that are challenging to capture using traditional methods.

In this paper, we propose a novel strategy for simulating the dynamics of elementary reactions using a quantum platform. We explore the superconducting circuit quantum electrodynamics (cQED) Kerr-cat device.^{25,28-34} We begin by introducing the Kerr-cat device and highlighting the features that make it ideally suited for analog simulations of chemical dynamics. Next, we consider examples of molecular systems to demonstrate its capabilities as applied to simulating proton transfer dynamics.

We begin by considering the effective Hamiltonian of the cQED Kerr-cat device, which constitutes of an arrangement of a few Josephson junctions schematically shown in Fig. 1:^{28,35}

$$\hat{H}_{KC} = \Delta \hat{a}^\dagger \hat{a} - K (\hat{a}^\dagger)^2 (\hat{a})^2 + \epsilon_2 (\hat{a}^2 + \hat{a}^{\dagger 2}) + \epsilon_1 (\hat{a} + \hat{a}^\dagger). \quad (1)$$

Here, \hat{a}^\dagger and \hat{a} are the ladder operators for the device bosonic mode, satisfying the usual bosonic commutator relation $[\hat{a}, \hat{a}^\dagger] = 1$. The Hamiltonian \hat{H}_{KC} includes adjustable parameters, namely the Kerr non-linearity, K , the detuning parameter, Δ , and the drive coefficients, ϵ_1 and ϵ_2 .

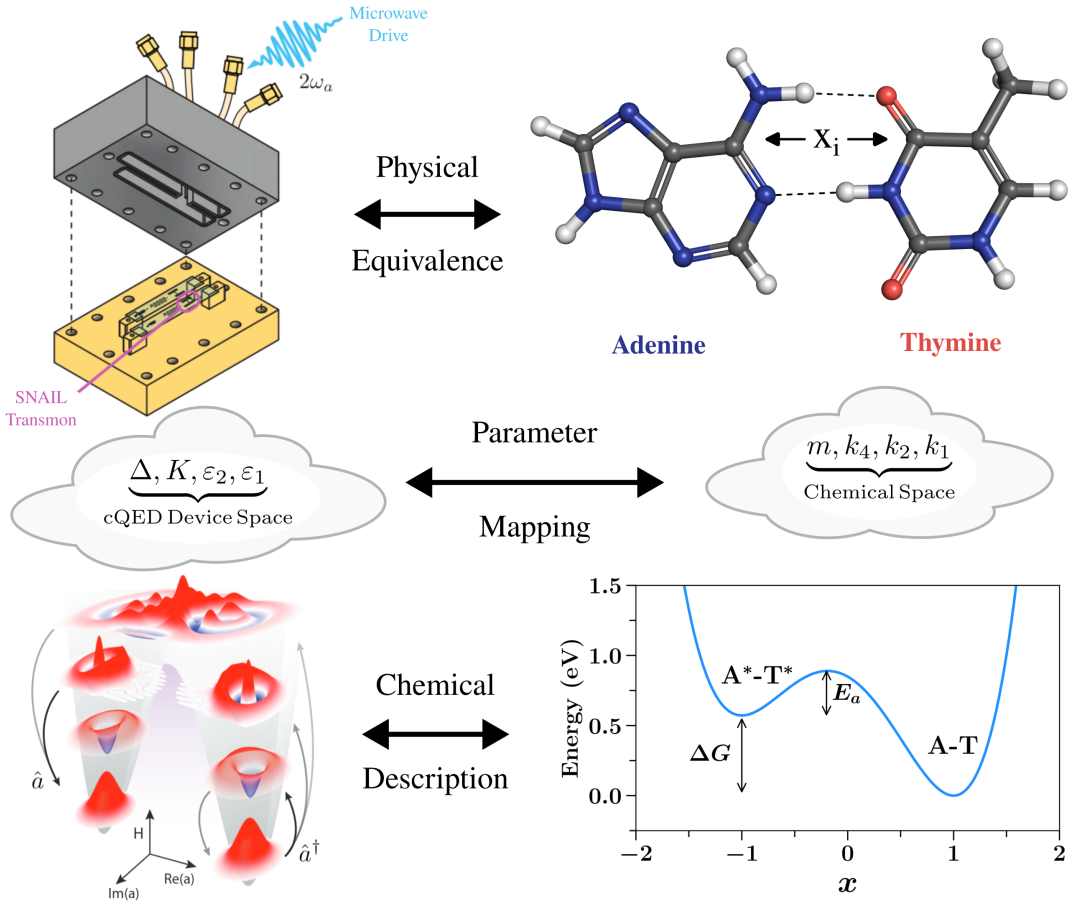


Figure 1: Schematic of Bosonic cQED Device for Quantum Dynamics Simulations in Hydrogen-Bonded Complexes (figure adapted from Ref. 25). The device is a half-aluminum, half-copper cavity resonator containing two sapphire chips with a SNAIL-transmon, readout resonator, and Purcell filter (top left). A strong microwave drive at twice the resonance frequency converts the SNAIL-transmon Hamiltonian into the bi-stable Kerr-cat parametric oscillator Hamiltonian for analog simulations of quantum dynamics in molecular systems, such as the adenine-thymine dimer (top right). Parameters $\Delta, K, \epsilon_1, \epsilon_2$ (middle left) are adjusted to map the effective Hamiltonian \hat{H}_{KC} to the double-well Hamiltonian modeling the molecular system (middle right). The bottom left shows the Wigner transform phase space representation of the device quantum states, which are analogous to the states in molecular the double-well potential in the bottom right.

Following Venkatraman *et al.*,²⁹ we assume that the dynamics of the device can be de-

scribed by the following Lindblad equation:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}_{KC}, \hat{\rho}] + \kappa (1 + n_{\text{th}}) \left(\hat{a} \hat{\rho} \hat{a}^\dagger - \frac{1}{2} \{ \hat{a}^\dagger \hat{a}, \hat{\rho} \} \right) + \kappa n_{\text{th}} \left(\hat{a}^\dagger \hat{\rho} \hat{a} - \frac{1}{2} \{ \hat{a} \hat{a}^\dagger, \hat{\rho} \} \right), \quad (2)$$

where κ sets the photon loss rate corresponding to an effective dissipation rate due to coupling of the system with a surrounding environment and n_{th} defines the effective temperature. Like $\{K, \Delta, \epsilon_1, \epsilon_2\}$, the parameters κ and n_{th} are experimentally tunable.³⁶

Consider also the model Hamiltonian for systems with a double-well potential energy surface given by

$$\hat{H}_{DW} = \frac{\hat{p}^2}{2m} + k_4 \hat{x}^4 - k_2 \hat{x}^2 + k_1 \hat{x}, \quad (3)$$

which is commonly used to simulate hydrogen bonded complexes.¹⁸ The position and momentum operators of the reaction coordinate, \hat{x} and \hat{p} , satisfy the commutation relation $[\hat{x}, \hat{p}] = i\hbar$. In the equation above, m represents the effective mass associated with motion along the reaction coordinate. The parameters $\{k_1, k_2, k_4\}$ are positive and real, typically determined by fitting the *ab initio* potential energy surface. This fitting process ensures the accurate representation of the barrier height, the curvature of the surface at the reactant and product wells, and the relative stability of reactants and products as parametrized by k_1 . Table 1 lists the parameters $\{k_1, k_2, k_4\}$ used in this study for simulations of proton transfer dynamics (with $m = 1836$ amu) in the four model systems illustrated in Fig. 2.

Table 1: Parameters used to simulate double-well potentials for proton transfer in molecular systems, according to the equation $V = k_4 x^4 - k_2 x^2 + k_1 x$.

System	k_4 [E_h/a_0^4]	k_2 [E_h/a_0^2]	k_1 [E_h/a_0]
Adenine-Thymine (DNA) ³⁷	1.4×10^{-3}	1.08×10^{-2}	5.2×10^{-3}
Guanine-Cytosine (DNA) ³⁸	7.7×10^{-4}	6.9×10^{-3}	4.5×10^{-3}
Malonaldehyde (cis-trans) ^{39,40}	9.4×10^{-5}	3.0×10^{-3}	2.9×10^{-3}
Malonaldehyde (cis-cis) ^{39,40}	7.1×10^{-4}	4.0×10^{-3}	0

The next step is to map the Kerr-cat Hamiltonian, introduced in Eq. (1), onto the

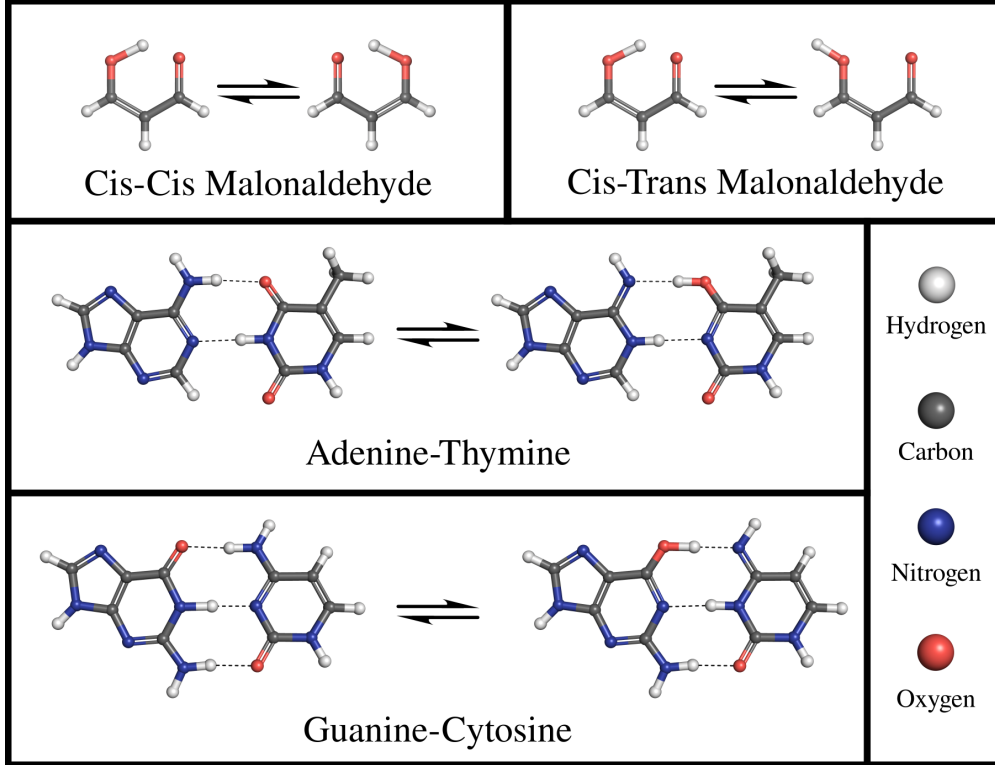


Figure 2: Hydrogen bonded complexes studied to analyze intramolecular proton transfer in cis-cis and cis-trans malonaldehyde (top), intramolecular proton transfer in adenine-thymine (amine, pyrimidine) (middle), and guanine-cytosine (amine, pyrimidine) base pairs.

model Hamiltonian of the molecular system presented in Eq. (3). This requires mapping the photonic operators, $\{\hat{a}, \hat{a}^\dagger\}$, onto the reaction coordinate operators, $\{\hat{x}, \hat{p}\}$. To ensure the correct dynamics, this mapping must preserve the commutation relations: $[\hat{x}, \hat{p}] = i\hbar$ and $[\hat{a}, \hat{a}^\dagger] = \hat{1}$. A mapping that satisfies these conditions is given by:

$$\hat{a} = \frac{1}{\sqrt{2}} \left(\frac{1}{c} \hat{x} + \frac{ic}{\hbar} \hat{p} \right), \quad \hat{a}^\dagger = \frac{1}{\sqrt{2}} \left(\frac{1}{c} \hat{x} - \frac{ic}{\hbar} \hat{p} \right), \quad (4)$$

where c is an arbitrary parameter with the same units as \hat{x} . Thus, the mapping of $\{\hat{a}, \hat{a}^\dagger\}$ onto $\{\hat{x}, \hat{p}\}$ is not unique. This flexibility in choosing c plays a crucial role in mapping the Kerr-cat Hamiltonian in Eq. (1) onto the chemical double-well Hamiltonian in Eq. (3). It should be noted that the value of c can be equivalent to the zero-point spread, $\sqrt{\hbar Z}$, if we define \hat{x} and \hat{p} as in reference 29.

Substituting the expressions for \hat{a} and \hat{a}^\dagger in terms of \hat{x} and \hat{p} from Eq. (4) into Eq. (1), we can recast the *negative* of the Kerr-cat Hamiltonian in terms of \hat{x} and \hat{p} , omitting constant terms that do not impact the dynamics:

$$\begin{aligned}
-\hat{H}_{KC} &= \frac{c^2}{\hbar^2} (\epsilon_2 - K - \Delta/2) \hat{p}^2 + \frac{K}{4c^4} \hat{x}^4 - \frac{1}{c^2} (\epsilon_2 + K + \Delta/2) \hat{x}^2 - \frac{\epsilon_1 \sqrt{2}}{c} \hat{x} \\
&+ \frac{Kc^4}{4\hbar^4} \hat{p}^4 + \frac{K}{4\hbar^2} (\hat{x}^2 \hat{p}^2 + \hat{p}^2 \hat{x}^2). \tag{5}
\end{aligned}$$

Comparing Eq. (5) with Eq. (3), we see that while $-\hat{H}_{KC}$ includes \hat{p}^2 , \hat{x}^4 , \hat{x}^2 and \hat{x} terms that can be mapped to the corresponding terms in the chemical double-well Hamiltonian (Eq. (3)), it also contains additional terms (\hat{p}^4 , $\hat{x}^2 \hat{p}^2$ and $\hat{p}^2 \hat{x}^2$) that are absent in Eq. (3).

We now map the parameters $\{\Delta, K, \epsilon_2, \epsilon_1\}$ onto $\{m, k_1, k_2, k_4\}$ by ensuring consistency between the \hat{p}^2 , \hat{x}^4 , \hat{x}^2 and \hat{x} terms in Eqs. (3) and (5). This leads to the following mapping relations:

$$K = 4c^4 k_4, \tag{6}$$

$$\epsilon_2 = \frac{\hbar^2}{4c^2 m} + \frac{c^2 k_2}{2}, \tag{7}$$

$$\Delta = -\frac{\hbar^2}{2c^2 m} + c^2 k_2 - 8c^4 k_4, \tag{8}$$

$$\epsilon_1 = -\frac{ck_1}{\sqrt{2}}. \tag{9}$$

Clearly, according to Eqs. (6)-(9), the values of $\{K, \Delta, \epsilon_1, \epsilon_2\}$ depend on the value of c . We then utilize the flexibility in choosing the value of c to minimize the effect of the additional terms \hat{p}^4 , $\hat{x}^2 \hat{p}^2$ and $\hat{p}^2 \hat{x}^2$ in Eq. (3). As demonstrated in the SI, this requires choosing a value of c small enough to satisfy the following inequality:

$$\frac{\hbar^2}{mk_2 c^4} \gg 1. \tag{10}$$

Next, we compare the energy levels of the Kerr-cat and double-well Hamiltonians, given

by Eq. (5) and Eq. (3), respectively. In general, these energy levels are expected to be *different* due to the additional terms \hat{p}^4 , $\hat{x}^2\hat{p}^2$ and $\hat{p}^2\hat{x}^2$ of the Kerr-cat Hamiltonian that are missing in the double-well Hamiltonian. However, the deviations between the energy levels of both Hamiltonians are expected to decrease as c becomes smaller [see Eq. (10) and Fig. 4, which is explained below].

To establish an acceptable value of c , we set the tolerance for deviations between the energy levels of the Kerr-cat and double-well Hamiltonians at $1.5 \text{ mE}_h = 0.941 \text{ kcal mol}^{-1}$, a standard measure of chemical accuracy. It is crucial to note that accurate descriptions of barrier crossing dynamics require this level of accuracy not only for the ground state but also for energy levels up to the top of the barrier.

For example, the number of states required to capture accurate dynamics in the molecular model systems analyzed in this work is as follows: 6 for cis-cis malonaldehyde (Fig. 3.A), 24 for cis-trans malonaldehyde (Fig. 3.B), 12 for adenine-thymine (Fig. 3.C), and 14 for guanine-cytosine (Fig. 3.D). Ensuring that the energy levels of the Kerr-cat device, E_{KC} , and chemical double-well Hamiltonians, E_{DW} , are within chemical accuracy of each other ($E_{KC} - E_{DW}$ is below the horizontal dashed line in the panels I of Fig. 4) also results in excellent agreement between their corresponding eigenfunctions, as shown in Fig. 3.

Using the cQED device to encode \hat{H}_{DW} requires a finite, non-zero value for the Kerr non-linearity K , so the units of Δ , ϵ_2 and ϵ_1 are expressed in terms of K . For vanishingly small values of c , the ratios $\frac{\Delta}{K}$, $\frac{\epsilon_2}{K}$, and $\frac{\epsilon_1}{K}$ become very large (panels II of Fig. 4), so they are experimentally unfeasible with current cQED platforms.⁴¹ However, there exists a range of values of c for which the parameters are experimentally accessible, while maintaining a useful degree of accuracy for the energies and stationary states. In particular, the Hamiltonian for the cis-cis malonaldehyde is both experimentally accessible and meets the chemical accuracy criterion for stationary states and energies (see Fig. 4A). Chemical systems with asymmetric free energy profiles pose greater challenges due to the higher number of eigenstates required for addressing kinetic questions. Expanding the range of experimental parameters could

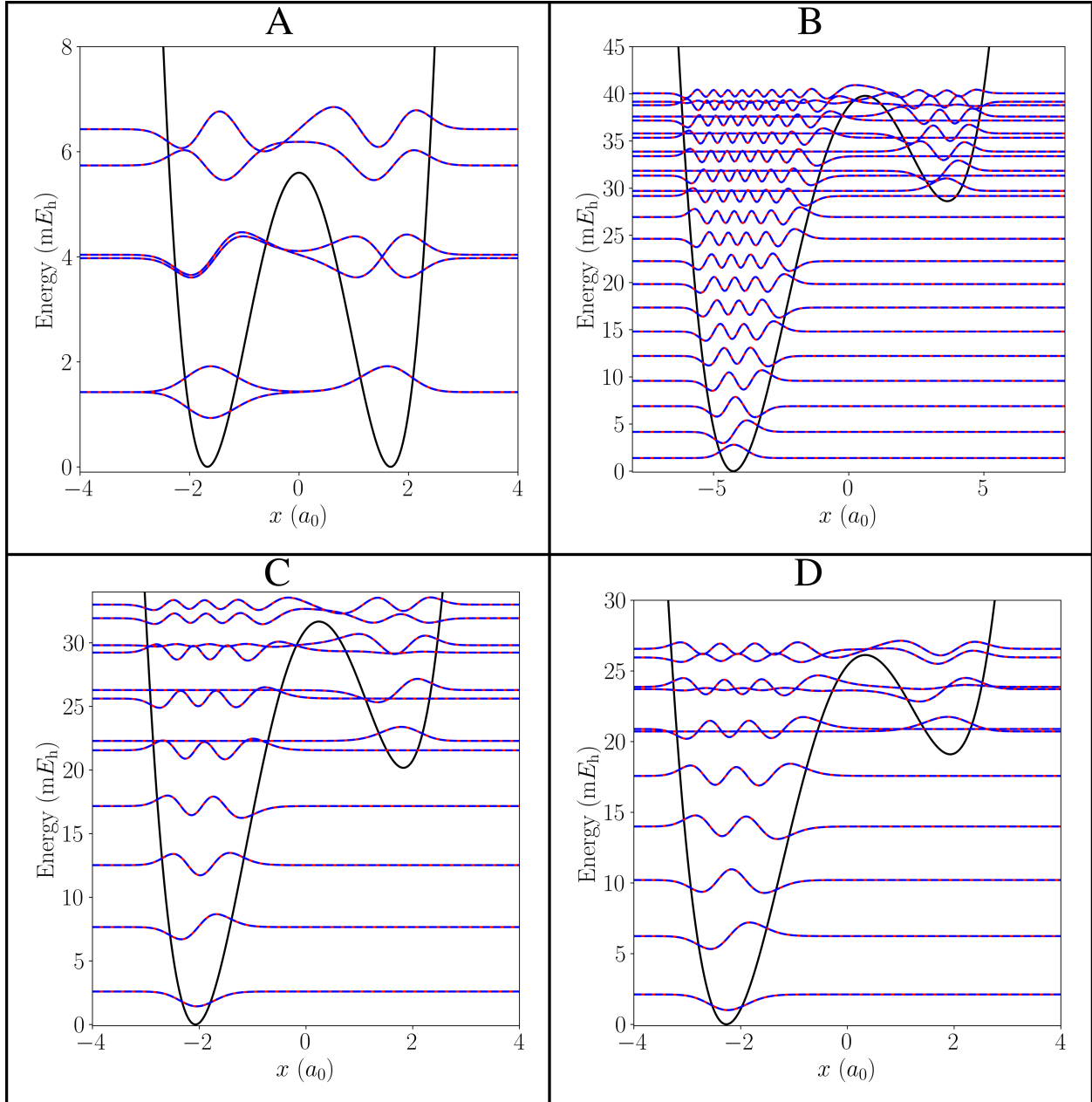


Figure 3: Eigenstates obtained by diagonalization of the model Hamiltonians for cis-cis malonaldehyde (A), cis-trans malonaldehyde (B), adenine-thymine (C), and guanine-cytosine (D), based on either the chemical double-well Hamiltonian (blue) or the Kerr-cat Hamiltonian (red) with $c = 0.1 a_0$. Eigenstates are shown together with the potential energy surface as a function of the reaction coordinate ‘ x ’.

enable an accurate simulation of these more challenging double-well problems, although it may also risk a breakdown of the effective Hamiltonian approximation.⁴¹

Consistency between the energy levels of the \hat{H}_{KC} and \hat{H}_{DW} Hamiltonians is necessary,

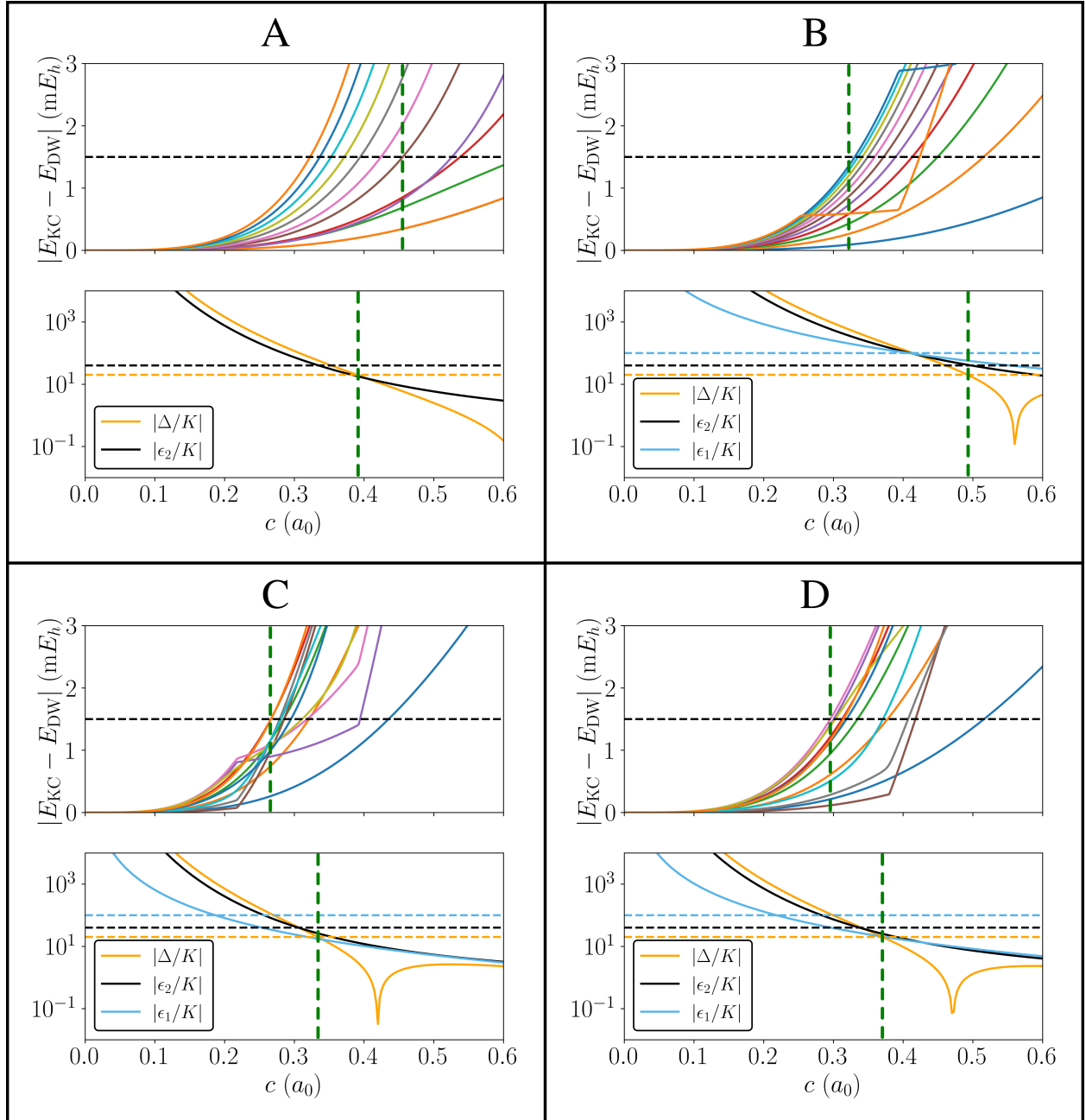


Figure 4: Absolute energy differences for the lower lying eigenstates of the chemical doublewell and Kerr-cat Hamiltonian (panels I) and cQED device parameters (panels II) as a function of the scaling parameter c for cis-cis malonaldehyde (A), cis-trans malonaldehyde (B), adenine-thymine (C) and guanine-cytosine (D). The horizontal black dashed line in panels I indicates the threshold of chemical accuracy at $1.5 mE_h$. The horizontal dashed lines in panels II indicate the maximum values of the parameters available in current cQED devices. The vertical dashed line indicates the maximum value of c recommended for accurate dynamics simulations (panels I) and minimum value of c ensuring experimental parameters available in existing cQED Kerr-cat platforms (panels II).⁴¹

but not sufficient to ensure that simulations on the Kerr-cat device accurately capture the chemical dynamics. This is because the *reaction rate* is also influenced by the coupling of the reaction coordinate to the thermal bath of *nonreactive* DOF. Consequently, the actual reaction rate constant depends not only on the eigenvalues and eigenfunctions of the Hamiltonian but also on the temperature and dissipation rate of the bath. Therefore, being able to simulate chemical dynamics on the Kerr-cat device requires that the dynamics of the device be dissipative, which is indeed the case. The Kerr-cat device is described by the Lindblad equation in Eq. (2) with adjustable photon loss rate constant κ and temperature set by n_{th} .

In what follows, we consider a chemical system that experiences the same type of dissipation as the Kerr-cat device. This dissipative model is useful as it results in chemical dynamics characterized by a reaction rate constant. However, other dissipation models could also be useful, as long as they capture the dissipation of the chemical system typically determined by the nature of its chemical environment and the way the reaction coordinate is coupled to the environment (*e.g.*, the surrounding can correspond to liquid solution, biological environment, or solid-state environment). Hence, characterizing the dissipation of specific chemical systems and replicating it on a Kerr-cat device remains a subject of future studies that will focus on bath engineering.^{42,43} It is noteworthy that Markovian and exotic dissipative channels can be engineered to a great extent in circuit QED.⁴⁴ The strength of dissipation in the squeezed Kerr oscillator experiment of Frattini and coworkers²⁸ is, for example, readily tunable by the amplitude of the microwave readout drive, and exotic forms of dissipation have been already demonstrated.^{45,46}

Assuming that the chemical system undergoes the same type of dissipation as the Kerr-cat device, we use Eq. (4) to express the dissipator in Eq. (2) in terms of the operators \hat{x} and \hat{p} , which form the basis of the chemical double-well Hamiltonian in Eq. (3). This results

in the following Lindblad equation for the chemical system:

$$\begin{aligned} \frac{\partial \hat{\rho}}{\partial t} = & -\frac{i}{\hbar} [\hat{H}_{DW}, \hat{\rho}] + \frac{\kappa(1+2n_{\text{th}})}{4} \left[\frac{1}{c^2} ([\hat{x}\hat{\rho}, \hat{x}] + [\hat{x}, \hat{\rho}\hat{x}]) + \frac{c^2}{\hbar^2} ([\hat{p}\hat{\rho}, \hat{p}] + [\hat{p}, \hat{\rho}\hat{p}]) \right] \\ & - \frac{i\kappa}{4\hbar} ([\hat{x}\hat{\rho}, \hat{p}] + [\hat{x}, \hat{\rho}\hat{p}] - [\hat{p}\hat{\rho}, \hat{x}] - [\hat{p}, \hat{\rho}\hat{x}]). \end{aligned} \quad (11)$$

The initial state for dynamics propagation is localized in the reactant well of the above-mentioned reactions. To generate this state, we diagonalize the system Hamiltonian and select the first eigenstate with more than 50% density in the reactant well. We then apply a sigmoidal filter function to remove the excess density outside of it (see SI for implementation details). This general localization method typically creates a localized Gaussian state and avoids the need to identify the critical points of each potential energy surface. By integrating Eq. (11) with an initial state $\hat{\rho}(0)$ localized in the reactant well, we obtain the time-evolved state $\hat{\rho}(t)$, which can be used to compute the product population at time t , as follows:

$$P_P(t) = \text{Tr}\{\hat{\rho}(t)\hat{\Theta}_X\}, \quad (12)$$

where $\hat{\Theta}_X$ is the Heaviside function:

$$\langle x|\hat{\Theta}_X|x'\rangle = \begin{cases} 0 & \text{for } x < 0, \\ \delta(x-x') & \text{for } x > 0. \end{cases} \quad (13)$$

The reactant-to-product reaction rate constant, $k = 1/T_X$, is obtained by fitting $P_P(t)$ to an exponential decay, as described below. The top subpanels of Fig. 5 show the time evolution of $P_P(t)$ for the four proton transfer reactions – cis malonaldehyde, cis-trans malonaldehyde, adenine-thymine, and guanine-cytosine – obtained by solving Eq. (11) for different values of c (solid lines). These top subpanels also include results where the chemical double-well Hamiltonian in Eq. (11), \hat{H}_{DW} , is replaced by the corresponding device Hamiltonian – \hat{H}_{KC} with additional terms \hat{p}^4 , $\hat{x}^2\hat{p}^2$ and $\hat{p}^2\hat{x}^2$ (diamonds). The bottom subpanels of Fig. 5 show

the dependence of the inverse reaction rate constant, T_X , on c for both \hat{H}_{DW} (solid line) and $-\hat{H}_{KC}$ (diamonds).

A close examination of the results in Fig. 5 reveals that the dynamics of both the chemical system and the Kerr-cat device align well with the rate kinetics described by a rate constant. Additionally, the reaction rate constant shows significantly less sensitivity to the value of c compared to the energy levels and eigenfunctions of \hat{H}_{DW} and \hat{H}_{KC} . Specifically, the rate constant predicted by the device matches that predicted for the chemical system at values of c as high as $0.4 a_0$, much higher than the value of $c = 0.1 a_0$ required to match energy levels and eigenfunctions near the top of the barrier. This is likely due to the effect of dissipation, making the overall dynamics less sensitive to small differences in the potential energy surface.

The results in Fig. 5 were obtained with $\kappa = 0.1$ and $n_{th} = 0.1$. However, the observed trends are insensitive to these specific values, as demonstrated by the rate constants obtained for various values of κ and n_{th} shown in Table 2 for $c = 0.1 a_0$. As expected, T_X increases (*i.e.*, the reaction slows down) when κ and n_{th} decrease. Nonetheless, the actual values of T_X for the chemical double-well and the Kerr-cat device are consistent, regardless of the κ and n_{th} values.

Table 2: Table of inverse reaction rate constants T_X (in \hbar/E_h) for each chemical system obtained with the \hat{H}_{DW} and \hat{H}_{KC} Hamiltonians, for various κ and n_{th} values with $c = 0.1 a_0$

Dissipation Constants (κ, n_{th})	(0.1, 0.1)	(0.1, 0.05)	(0.025, 0.1)	(0.025, 0.05)
Cis-cis Malonaldehyde (KC)	91 ± 1	91 ± 1	303 ± 4	295 ± 4
Cis-cis Malonaldehyde (DW)	91 ± 1	91 ± 1	303 ± 4	295 ± 4
Cis-trans Malonaldehyde (KC)	147 ± 2	142 ± 2	527 ± 7	499 ± 6
Cis-trans Malonaldehyde (DW)	147 ± 2	142 ± 2	528 ± 7	500 ± 6
Adenine-Thymine (KC)	95 ± 1	94 ± 1	323 ± 4	314 ± 4
Adenine-Thymine (DW)	95 ± 1	94 ± 1	323 ± 4	314 ± 4
Guanine-Cytosine (KC)	96 ± 1	95 ± 1	325 ± 4	316 ± 4
Guanine-Cytosine (DW)	96 ± 1	95 ± 1	325 ± 4	316 ± 4

Conclusions.– In this paper, we proposed a novel approach to simulating chemical dy-

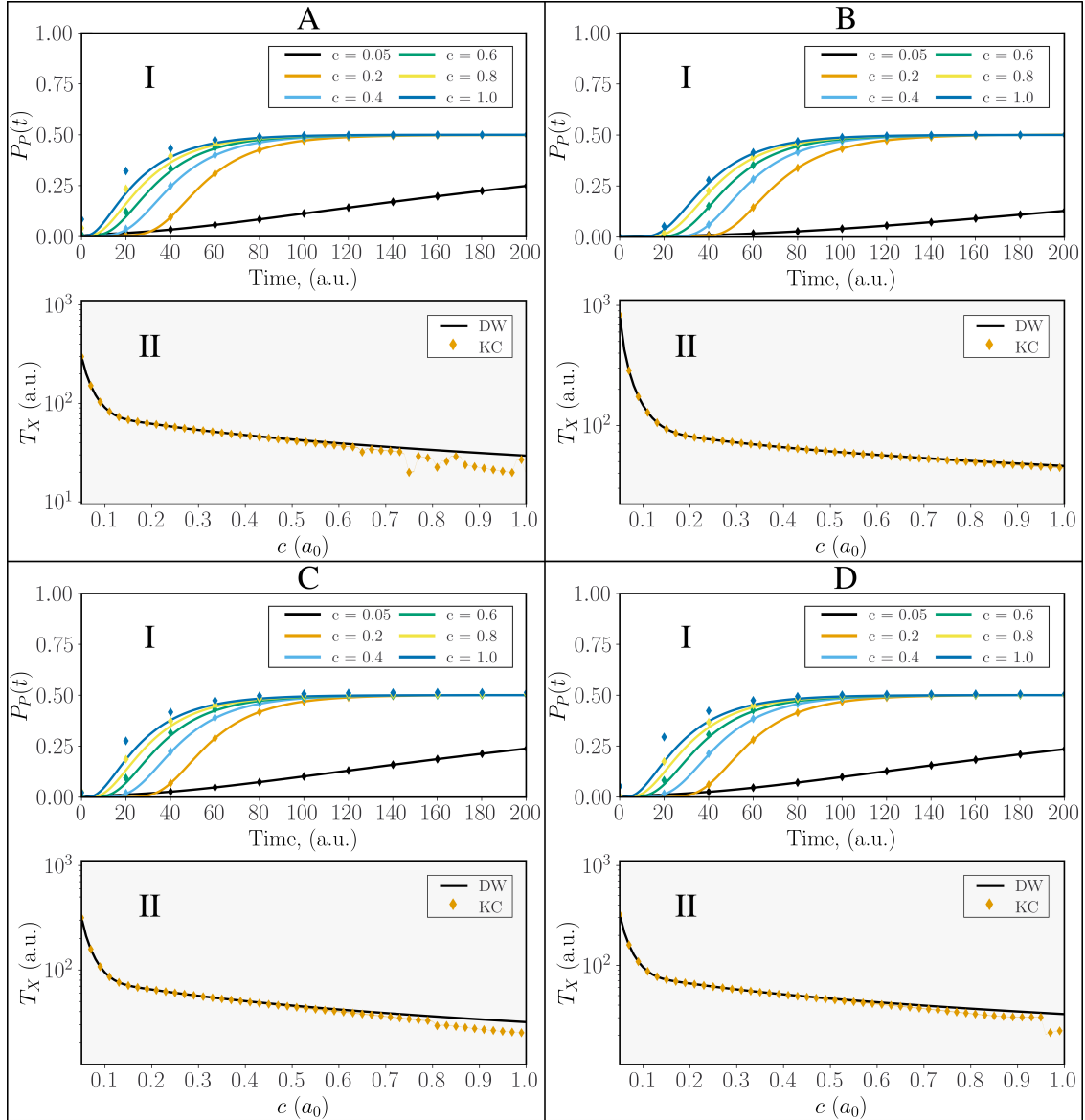


Figure 5: Comparison of observables obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.1$ and $n_{th} = 0.1$, for cis-cis malonaldehyde (A), cis-trans malonaldehyde (B), adenine-thymine (C) and guanine-cytosine (D). The time evolution of the product population is shown in the top subpanels (I), while the corresponding inverse reaction rate constants are shown in the bottom subpanels (II).

namics using a tunable Kerr-cat quantum device. This method allows for precise control over the parameters defining double-well potential energy surfaces, as well as external factors such as temperature and dissipation rates. We demonstrated the efficacy of this approach by applying it to proton transfer in four prototypical hydrogen-bonded model complexes, showing

that the underlying chemical dynamics can be accurately simulated on a quantum device.

Simulating chemical dynamics on a Kerr-cat device requires overcoming several challenges. A primary challenge, addressed in this paper, is mapping the chemical double-well Hamiltonian onto the Kerr-cat device Hamiltonian. This mapping is nontrivial, because the Kerr-cat device Hamiltonian includes additional terms (\hat{p}^4 , $\hat{x}^2\hat{p}^2$ and $\hat{p}^2\hat{x}^2$), that are absent in the chemical Hamiltonian. We resolved this challenge by introducing a method that minimizes the impact of those additional terms by adjusting the parameter c in the mapping of the photonic operators \hat{a} and \hat{a}^\dagger to the chemical operators \hat{x} and \hat{p} . Specifically, we demonstrated that the energy levels and stationary states of the Kerr-cat and chemical Hamiltonians can be aligned (within chemical accuracy tolerance) by selecting a sufficiently small value of c . Furthermore, we found that reaction rate constants are even less sensitive to the value of c than the energy levels and stationary states, making them easier to reproduce when simulating chemical dynamics on the Kerr-cat device.

The approach proposed in this paper represents a significant first step towards enabling simulations of chemical dynamics on bosonic quantum simulators, which is beyond the capabilities of currently available NISQ computers. Remaining challenges include characterizing and engineering dissipation, and designing devices that can reliably emulate more complex free energy surfaces beyond the one-dimensional asymmetric double-well free energy surfaces considered in this paper. Ongoing work addressing these challenges will be reported in future papers, paving the way for even more advanced simulations of quantum chemical dynamics on quantum devices.

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Supporting Information Available

Includes a detailed description of the methods and additional figures.

Code and Data Availability

The Python code for the Hamiltonian analysis and dynamical simulations can be found at <https://github.com/dcabral00/cQED4ChemDyn>. The data files used to generate the figures in the manuscript are also provided at <https://github.com/dcabral00/cQED4ChemDyn> and hosted at Zenodo.⁴⁷

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Supporting Information for
”A Roadmap for Simulating Chemical Dynamics On A
Parametrically Driven Bosonic Quantum Device”

Mapping the Device Hamiltonian to Chemical Double-Well

We start out by considering the following general Hamiltonian which is suitable for modeling the dynamics of a wide range of elementary chemical reactions:

$$\hat{H}_{DW} = \frac{\hat{p}^2}{2m} + k_4\hat{x}^4 - k_2\hat{x}^2 + k_1\hat{x} \quad . \quad (14)$$

Here, \hat{x} and \hat{p} are the position and momentum operators associated with motion along the reaction coordinate, which satisfy $[\hat{x}, \hat{p}] = i\hbar$; m is the mass associated with the motion along the reaction coordinate; and $\{k_1, k_2, k_4\}$ are positive and real parameters whose values define the double well free energy profile, and thereby the specific chemical system, that the Hamiltonian describes. More specifically, given the double-well free energy profile for a specific chemical system, which can be obtained from electronic structure and MD simulations,¹⁴ we assume that it can be fitted to a minimal fourth-order polynomial of the form $V(x) = k_4x^4 - k_2x^2 + k_1x$. The $k_4x^4 - k_2x^2$ term is necessary for obtaining the double-well feature, while the k_1x term is necessary in order to account for asymmetry between the reactant and product wells ($k_1 = 0$ gives rise to a symmetrical double-well free energy profile, which corresponds to an iso-energetic chemical reaction for which $\Delta G = 0$). It should be noted that a third order x^3 term is excluded. This is necessary for mapping onto the Hamiltonian of currently accessible experimental Kerr-Cat devices (see below), and justified by the fact that adding a x^3 term is not necessary for capturing the main features associated with a chemical reaction, namely an asymmetrical double-well profile. It should also be noted that a description of the chemical dynamics in terms of a TST/Arrhenius-like rate constant requires coupling the reaction coordinate to a thermal bath of nonreactive DOF in order to

make activation to the transition state and barrier crossing possible, followed by equilibration in the product well before significant recrossing can occur (see below). We consider the

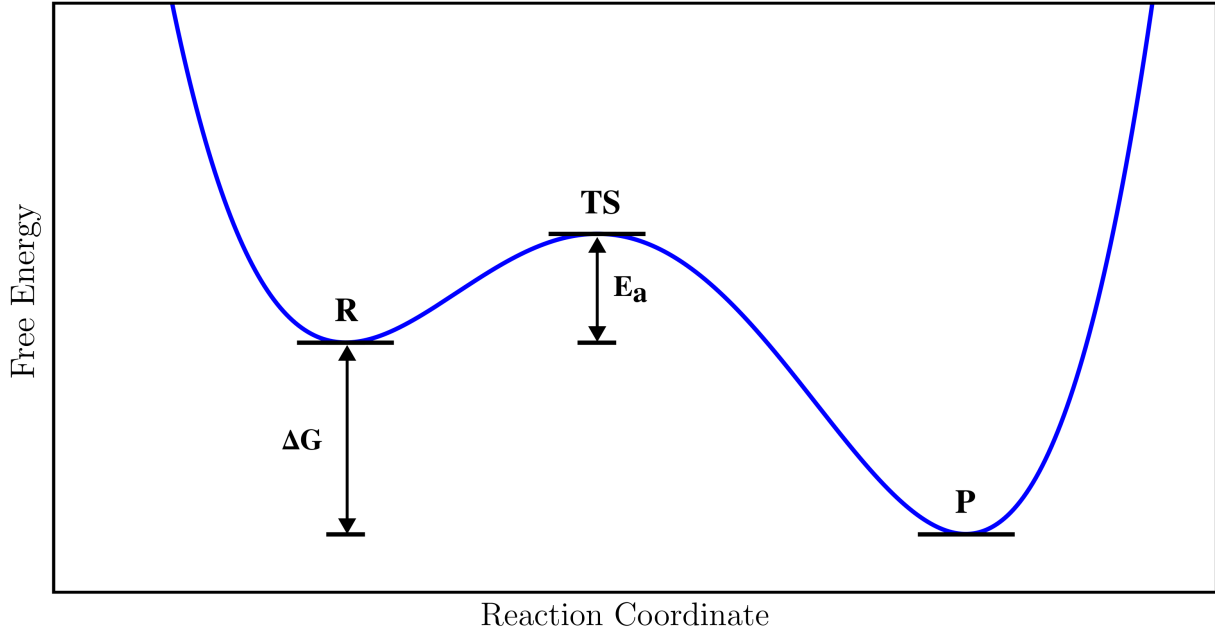


Figure 6: A schematic view of the the free energy double-well profile, $V(x)$, along the reaction coordinate, x . The reactant and product wells are designated by R and P , respectively. The transition state, which corresponds to the barrier top, is designated by TS . E_a and ΔG are the activation energy and reaction free energy, respectively. It should be noted that the reaction coordinate needs to be coupled to a thermal bath of nonreactive DOF (not shown) in order for rate kinetics to be emerge.

effective Hamiltonian for currently experimentally realizable parametrically-driven Kerr-Cat cQED devices, which is given by:^{28–32,48}

$$\hat{H}_{KC} = \Delta \hat{a}^\dagger \hat{a} - K (\hat{a}^\dagger)^2 (\hat{a})^2 + \epsilon_2 (\hat{a}^2 + \hat{a}^{\dagger 2}) + \epsilon_1 (\hat{a} + \hat{a}^\dagger) . \quad (15)$$

Here, \hat{a} and \hat{a}^\dagger are (unit-less) photonic creation and annihilation operators associated with the electromagnetic mode supported by the cavity, which satisfy $[\hat{a}, \hat{a}^\dagger] = \hat{1}$, and $\{\Delta, K, \epsilon_2, \epsilon_1\}$ are experimentally controllable parameters (all given in terms of energy units). Noting that the double-well and Kerr-Cat Hamiltonians in Eqs. (14) and (15), respectively, are both given by fourth-order polynomials determined by four free parameters ($\{m, k_1, k_2, k_4\}$ and $\{\Delta, K, \epsilon_2, \epsilon_1\}$, respectively), our goal in the next step is to map the Kerr-Cat Hamiltonian

in Eq. (15), onto the chemical double-well Hamiltonian in Eq. (14).

To this end, we first need to map the photonic operators, $\{\hat{a}, \hat{a}^\dagger\}$ onto the operators associated with motion along the reaction coordinate, $\{\hat{x}, \hat{p}\}$. To generate the correct dynamics, the mapping needs to be consistent with the corresponding commutators: $[\hat{x}, \hat{p}] = i\hbar$ and $[\hat{a}, \hat{a}^\dagger] = \hat{1}$. A mapping that satisfies this is given by:

$$\begin{aligned}\hat{a} &= \frac{1}{\sqrt{2}} \left(\frac{1}{c} \hat{x} + \frac{ic}{\hbar} \hat{p} \right) \quad ; \quad \hat{a}^\dagger = \frac{1}{\sqrt{2}} \left(\frac{1}{c} \hat{x} - \frac{ic}{\hbar} \hat{p} \right) \\ \hat{x} &= \frac{c}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger) \quad ; \quad \hat{p} = \frac{\hbar}{i\sqrt{2}c} (\hat{a} - \hat{a}^\dagger) \quad .\end{aligned}\tag{16}$$

Here, c is a constant parameter that has units of length (same units as \hat{x}). Importantly, the value of c is arbitrary in the sense that the commutators $[\hat{x}, \hat{p}] = i\hbar$ and $[\hat{a}, \hat{a}^\dagger] = \hat{1}$ are invariant to the choice of c . In other words, the mapping of $\{\hat{a}, \hat{a}^\dagger\}$ onto $\{\hat{x}, \hat{p}\}$ is not unique. As we will see below, this flexibility with respect to the choice of c plays an crucial role in mapping the Kerr-Cat Hamiltonian in Eq. (15), onto the chemical double-well Hamiltonian in Eq. (14).

Substituting the expressions for \hat{a} and \hat{a}^\dagger in terms of \hat{x} and \hat{p} from Eq. (16) into Eq. (15), we can recast the *negative* of the Kerr-Cat Hamiltonian in terms of the \hat{x} and \hat{p} (dropping constant terms which do not impact the dynamics):

$$\begin{aligned}-\hat{H}_{KC} &= \frac{c^2}{\hbar^2} (\epsilon_2 - K - \Delta/2) \hat{p}^2 + \frac{K}{4c^4} \hat{x}^4 - \frac{1}{c^2} (\epsilon_2 + K + \Delta/2) \hat{x}^2 - \frac{\epsilon_1 \sqrt{2}}{c} \hat{x} \\ &+ \frac{Kc^4}{4\hbar^4} \hat{p}^4 + \frac{K}{4\hbar^2} \hat{x}^2 \hat{p}^2 + \frac{K}{4\hbar^2} \hat{p}^2 \hat{x}^2\end{aligned}\tag{17}$$

Comparing Eq. (17) with Eq. (14), we see that while $-\hat{H}_{KC}$ contains \hat{p}^2 , \hat{x}^4 , \hat{x}^2 and \hat{x} terms which can be mapped onto the corresponding terms in the chemical double-well Hamiltonian in Eq. (14), it also contains spurious \hat{p}^4 , $\hat{x}^2 \hat{p}^2$ and $\hat{p}^2 \hat{x}^2$ terms that lack counterparts in Eq. (14).

In the next step, we map $\{\Delta, K, \epsilon_2, \epsilon_1\}$ onto $\{m, k_1, k_2, k_4\}$ by requiring consistency be-

tween the \hat{p}^2 , \hat{x}^4 , \hat{x}^2 and \hat{x} terms in Eqs. (14) and (17), which leads to the following mapping relations:

$$K = 4c^4k_4 \quad (18)$$

$$\epsilon_2 = \frac{\hbar^2 + 2c^4k_2m}{4c^2m} \quad (19)$$

$$\Delta = \frac{2c^4k_2m - \hbar^2 - 16c^6k_4m}{2c^2m} \quad (20)$$

$$\epsilon_1 = -\frac{ck_1}{\sqrt{2}} \quad (21)$$

We also take advantage of the aforementioned flexibility in choosing the value of c to minimize the effect of the spurious \hat{p}^4 , $\hat{x}^2\hat{p}^2$ and $\hat{x}^2\hat{p}^2$ terms in Eq. (14). As we show below, doing so requires that we choose a value of c small enough so that it satisfies the following inequality:

$$\frac{\hbar^2}{mk_2c^4} \gg 1 \quad (22)$$

To derive the inequality in Eq. (22), we note that the \hat{x}^4 , \hat{x}^2 and \hat{x} terms in Eq. (17) become *larger* relative to the other terms with *decreasing* c . This suggests that choosing a sufficiently small value of c can make the spurious p^4 , x^2p^2 and x^2p^2 terms negligible. However, the fact the kinetic energy term in Eq. (17), $\frac{c^2}{\hbar^2}(\epsilon_2 - K - \Delta/2)\hat{p}^2$, also decreases with decreasing c implies that the value of c also needs to be chosen such that the spurious terms will be negligible compared to it. It must be noted that if one puts Eq. 18-21 in units of K , that being $\{\epsilon_1/K, \epsilon_2/K, \Delta/K\}$, these quantities diverge when $\lim c \rightarrow 0$, with these quantities getting quite large when c is small. So, it is necessary to pick a value of c which produces experimentally accessible values of $\{\epsilon_1/K, \epsilon_2/K, \Delta/K\}$ for a given chemical system while ensuring sufficient chemical accuracy.

To this end, we consider the the symmetrical double-well case ($k_1 = 0$), for which it can be shown that the reactant and product equilibrium geometries are given by $\pm x_0$, where $x_0 = \sqrt{\frac{k_2}{2k_4}}$ and the activation energy is given by $E_a = \frac{k_2^2}{4k_4}$. Thus, $\{x_0, E_a\}$ are interchangeable

with $\{k_2, k_4\}$ in this case, such that Eq. (18) becomes $K = \frac{4E_a c^4}{x_0^4}$. Hence,

$$\frac{K}{4\hbar^2} \left[\frac{c^4}{\hbar^2} \hat{p}^4 + \hat{x}^2 \hat{p}^2 + \hat{p}^2 \hat{x}^2 \right] \rightarrow \frac{E_a c^4}{\hbar^2 x_0^4} \left[\frac{c^4}{\hbar^2} \hat{p}^4 + \hat{x}^2 \hat{p}^2 + \hat{p}^2 \hat{x}^2 \right] \quad (23)$$

Given that x_0 set the length scale of the chemical system, one can estimate the order of magnitude of the $\hat{x}^2 \hat{p}^2$ and $\hat{p}^2 \hat{x}^2$ terms to be $\frac{E_a c^4}{\hbar^2 x_0^4} x_0^2 \hat{p}^2 = \frac{E_a c^4}{\hbar^2 x_0^2} \hat{p}^2$. Thus, requiring that the spurious $\hat{x}^2 \hat{p}^2$ and $\hat{p}^2 \hat{x}^2$ terms are negligible relative to the kinetic energy term, $\frac{\hat{p}^2}{2m}$ gives rise to the inequality $\frac{E_a c^4}{\hbar^2 x_0^2} \hat{p}^2 \ll \frac{1}{2m} \hat{p}^2$, which can be rearranged to give $\frac{\hbar^2 x_0^2}{2m E_a c^4} \gg 1$. Noting that $k_2 = \frac{2E_a}{x_0}$ then leads to the inequality in Eq. (22).

The fact that the \hat{p}^4 term scales like c^4 , while the \hat{p}^2 term scales like c^2 , also implies that the \hat{p}^4 will become negligible for a sufficiently small value of c . In fact, the same inequality, Eq. (22), can be derived by noting that $\frac{1}{2m} \hat{p}^2 \gg \frac{E_a c^8}{\hbar^4 x_0^4} \hat{p}^4$ is equivalent to $\frac{1}{2m} \gg \frac{E_a c^8}{\hbar^4 x_0^4} \hat{p}^2$ and noting that the momentum is maximal when the particle is around the minima, where the potential energy can be approximated as being harmonic. Invoking the virial theorem for the harmonic oscillator, according to which the expectation values of the kinetic energy is equal to that of the potential energy, and noting that E_a sets the potential energy scale for the chemical system, we can then estimate \hat{p}^2 by $2mE_a$ in the inequality $\frac{1}{2m} \gg \frac{E_a c^8}{\hbar^4 x_0^4} \hat{p}^2$, which turns it into the inequality $\left(\frac{\hbar^2 x_0^2}{2m E_a c^4} \right)^2 \gg 1$. Thus, satisfying the inequality in Eq. (22), which is equivalent to $\frac{\hbar^2 x_0^2}{2m E_a c^4} \gg 1$, also guarantees that the \hat{p}^4 term will become negligible compared to the \hat{p}^2 kinetic energy term.

Finally, the argument for why the same argument would also hold for an *asymmetrical* double-well has to do with the expectation that the length and energy scales of the chemical system are not going to be significantly affected by the addition of the asymmetry.

Computational Methods

In this work, we examine the dissipative dynamics of the asymmetric Kerr-Cat Hamiltonian,

$$\frac{\hat{H}}{\hbar} = \Delta \hat{a}^\dagger \hat{a} - K (\hat{a}^\dagger)^2 (\hat{a})^2 + \epsilon_2 (\hat{a}^2 + \hat{a}^{\dagger 2}) + \epsilon_1 (\hat{a} + \hat{a}^\dagger), \quad (24)$$

where Δ , ϵ_2 , ϵ_1 control the potential landscape parameters such as inter-well separation, barrier height, and well asymmetry, respectively. The entire Hamiltonian is scaled by K , which is taken to be a constant value throughout the manuscript, unless otherwise stated. The operators a^\dagger, a are the quantum Harmonic oscillator excitation and de-excitation operators expressed in the basis of Fock states. To simulate the dissipative dynamics of this Hamiltonian, we use the Lindblad master equation:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}(t)] + \mathcal{D}[\hat{\rho}(t)], \quad (25)$$

where \hat{H} is the Kerr-Cat Hamiltonian, $\hat{\rho}(t)$ is the time-dependent density matrix and $\mathcal{D}[\hat{\rho}(t)]$ is the dissipator defined as:

$$\mathcal{D}[\hat{\rho}(t)] = \kappa(1 + n_{\text{th}}) \left(\hat{a} \hat{\rho} \hat{a}^\dagger - \frac{1}{2} \{ \hat{a}^\dagger \hat{a}, \hat{\rho} \} \right) + \kappa n_{\text{th}} \left(\hat{a}^\dagger \hat{\rho} \hat{a} - \frac{1}{2} \{ \hat{a} \hat{a}^\dagger, \hat{\rho} \} \right) \quad (26)$$

with a^\dagger, a being excitation and deexcitation operators, whose effect is governed by the magnitude of the thermal parameters κ and n_{th} . To implement the Lindblad equation and simulate dissipative dynamics, we vectorize the density matrix and matricize the Lindbladian, using the relationship $\text{vec}(AXB) = (B^T \otimes A)\text{vec}(X)$, such that

$$\frac{\partial \hat{\rho}}{\partial t} = \hat{\mathcal{L}} \hat{\rho} \quad (27)$$

Thus, we must find a suitable representation for $\hat{\mathcal{L}}$. We introduce identity matrices to utilize the vectorization relationship and apply it to the Hamiltonian:

$$\left[\hat{H}, \hat{\rho}(t) \right] = \hat{H} \hat{\rho} \mathbb{I} - \mathbb{I} \hat{\rho} \hat{H} \quad (28)$$

$$= \left(\mathbb{I} \otimes \hat{H} - \hat{H}^T \otimes \mathbb{I} \right) \hat{\rho} \quad (29)$$

Similarly, we can alter the dissipator:

$$\begin{aligned} \mathcal{D}[\hat{\rho}(t)] &= \kappa(1 + n_{\text{th}}) \left(\hat{a} \hat{\rho} \hat{a}^\dagger - \frac{1}{2} (\hat{a}^\dagger \hat{a} \hat{\rho} \mathbb{I} + \mathbb{I} \hat{\rho} \hat{a}^\dagger \hat{a}) \right) \\ &\quad + \kappa n_{\text{th}} \left(\hat{a}^\dagger \hat{\rho} \hat{a} - \frac{1}{2} (\hat{a} \hat{a}^\dagger \hat{\rho} \mathbb{I} + \mathbb{I} \hat{\rho} \hat{a} \hat{a}^\dagger) \right) \end{aligned} \quad (30)$$

$$\begin{aligned} &= \kappa(1 + n_{\text{th}}) \left(\hat{a}^* \otimes \hat{a} - \frac{1}{2} (\mathbb{I} \otimes \hat{a}^\dagger \hat{a} + \hat{a}^T \hat{a}^* \otimes \mathbb{I}) \right) \hat{\rho} \\ &\quad + \kappa n_{\text{th}} \left(\hat{a}^T \otimes \hat{a}^\dagger - \frac{1}{2} (\mathbb{I} \otimes \hat{a} \hat{a}^\dagger + \hat{a}^* \hat{a}^T \otimes \mathbb{I}) \right) \hat{\rho} \end{aligned} \quad (31)$$

Reassembling the complete matricized Lindblad equation, we obtain

$$\begin{aligned} \dot{\hat{\rho}} &= \left(\mathbb{I} \otimes \hat{H} - \hat{H}^T \otimes \mathbb{I} \right. \\ &\quad + \kappa(1 + n_{\text{th}}) \left(\hat{a}^* \otimes \hat{a} - \frac{1}{2} (\mathbb{I} \otimes \hat{a}^\dagger \hat{a} + \hat{a}^T \hat{a}^* \otimes \mathbb{I}) \right) \\ &\quad \left. + \kappa n_{\text{th}} \left(\hat{a}^T \otimes \hat{a}^\dagger - \frac{1}{2} (\mathbb{I} \otimes \hat{a} \hat{a}^\dagger + \hat{a}^* \hat{a}^T \otimes \mathbb{I}) \right) \right) \hat{\rho} \end{aligned} \quad (32)$$

To simulate the population dynamics, we integrate equation 27,

$$\hat{\rho}_t = \hat{\rho}(t) = e^{\hat{\mathcal{L}}t} \hat{\rho}_0 \quad (33)$$

and calculate the action of time-evolution of the Lindbladian operator on the propagated density matrix for a small time-step $\tau = 0.1$:

$$\hat{\rho}(t) = e^{\hat{\mathcal{L}}\tau} \hat{\rho}(t - \tau) \quad (34)$$

The matrix exponential operator is implemented using the `scipy.linalg.expm` routine, which implements a scaling and squaring algorithm based on Pade's approximation.⁴⁹

Initial State

The initial state of the system is crucial to the dynamics. We start by diagonalizing the Hamiltonian H to find the eigenstate matrix Φ of the system in the harmonic oscillator Fock basis:

$$H\Phi = \lambda\Phi \quad (35)$$

We then find the grid-based position representation (x) of the individual eigenstates, ϕ_i , using the quantum Harmonic oscillator basis set:

$$\phi_i = \sum_n^N c_{n,i} \psi_n(x) \quad (36)$$

Where $c_{n,i}$ indicate the expansion coefficients associated with eigenstate i and using N harmonic oscillator functions of the form

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} H_n \left(\sqrt{\frac{m\omega}{\hbar}} x\right), \quad n = 0, 1, 2, \dots \quad (37)$$

In this expression, n indicates the order of the basis function, m represents the mass, ω is the fundamental frequency of the oscillator, \hbar is the reduced Planck's constant and H_n are the

physicist's Hermite polynomials of order n , which follow the following recurrence relation:

$$\left\{ \begin{array}{l} H_0(x) = 1 \\ H_1(x) = 2x \\ \vdots \\ H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x) \end{array} \right.$$

We select a suitable initial state by finding the first state with more than 50% amplitude on the desired portion of the potential energy surface (figure 7, left panel) and then convolve it with a sigmoidal filter function of the form:

$$S(x; x_0, t) = \frac{1}{1 + e^{-(x-x_0)/t}}, \quad (38)$$

where x indicates the position, x_0 indicates the cutoff position and t the smoothness of the function near the cutoff. We observe that the Heaviside function, $\Theta(x; x_0) = 1$ if $x \geq x_0$ else $\Theta(x; x_0) = 0$, is recovered when taking $\lim_{t \rightarrow 0} S(x; x_0, t)$. This allows localization of the initial state in position space which we then convert it back to the Fock basis representation (figure 7, right panel). All dynamics trajectories use eigenstate selection with a sigmoidal filter with a tail of 0.5.

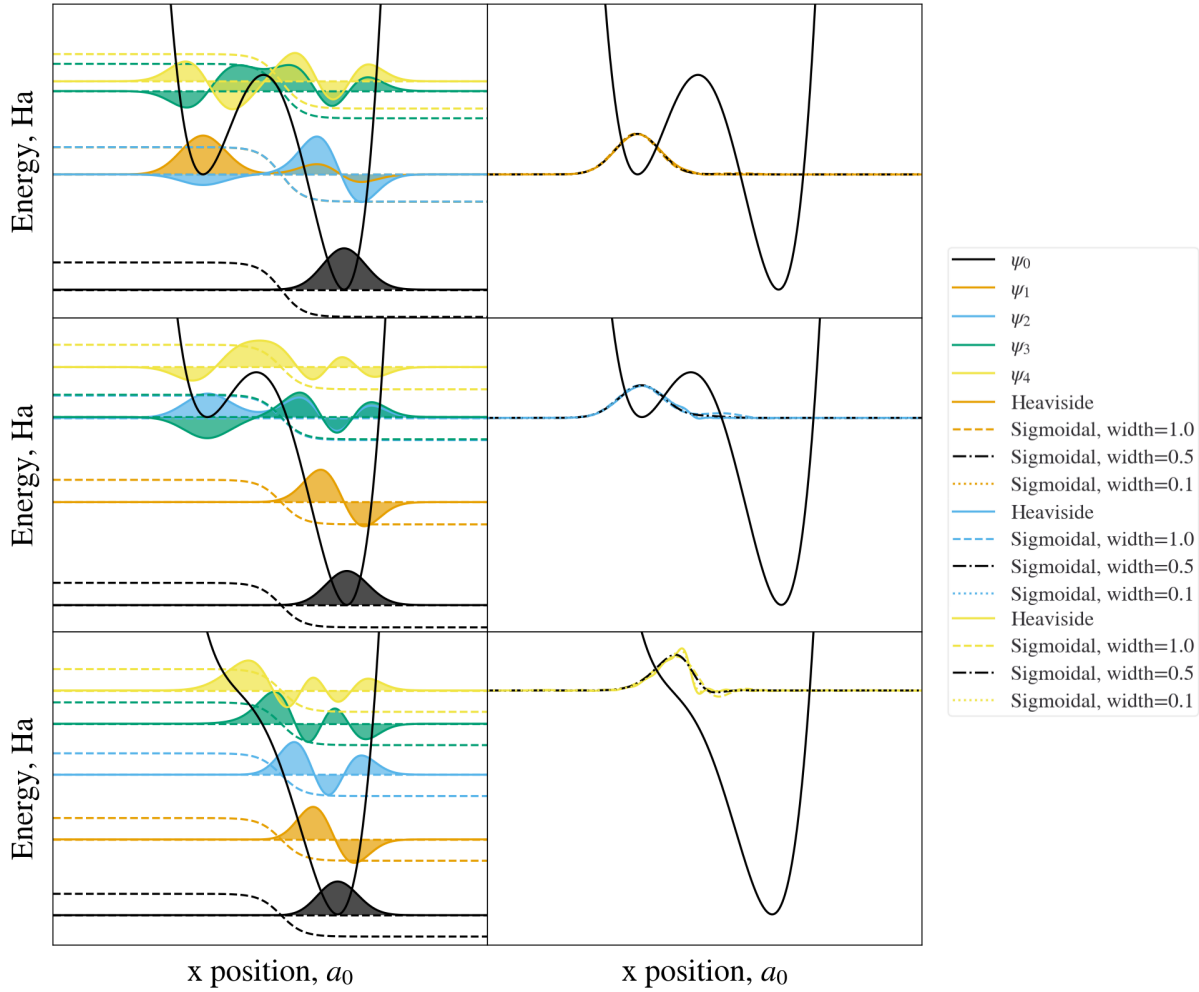


Figure 7: Initial state selection for three different values of ϵ_1, ϵ_2 by applying a sigmoidal or Heaviside filtering function. The procedure is illustrated for the first 5 eigenstates, plotted with the metapotential on the background to showcase how the localization scheme performs. The right side showcases the effect of the different filter parameters as applied to the most suitable state that contains more than 50% density on the top well. Higher values of the sigmoidal tail value reduce initial state localization, while higher values introduce oscillatory motions due to the verticality of the filter function near its center.

Dynamics Subspace

The accuracy of the dynamics is dependent on the number of Fock basis states used. However, the size of the Lindbladian matrix scales as $\mathcal{O}(N^4)$ with the number of Fock states as compared to the Hamiltonian $\mathcal{O}(N^2)$, which makes matrix exponentiation (performed once for each set of Hamiltonian parameters) and multiplication (performed for each timestep in a trajectory) a limiting factor in simulation. Thus, we generate the complete Hamiltonian with a large number of Fock states ($N=300$) and numerically diagonalize to obtain accurate eigenvalues and eigenvectors and use the first $M=20$ states to perform a similarity transformation matrix to reduce the dynamics computational space:

$$H_{N \times N} C_{N \times N} = \lambda_{N \times N} C_{N \times N} \rightarrow D_{N \times M} \equiv C_{N \times M} \quad (39)$$

Where $\lambda_{N \times N}$, $C_{N \times N}$ contains the eigenvalues, eigenvectors of the Hamiltonian $H_{N \times N}$ in the full N -dimensional space and $C_{N \times M}$ represent the reduced dimensionality eigenvector matrix containing the first M eigenstates which is defined as the transformation matrix $D_{N \times M}$. Then the initial state ($\hat{\rho}_0$), the Hamiltonian (H) and the Lindbladian ladder operators (a^\dagger, a) are transformed into the reduced Hilbert space according to the transformation,

$$A'_{M \times M} = D_{M \times N}^T A_{N \times N} D_{N \times M} \quad (40)$$

As a consequence of this, the ladder operators now encode information about the properties of the Hamiltonian and thus can better simulate the dynamics of the system.

Observables

For this work, we focus on observables corresponding to traces with the time-evolved state. These include traces with the initial state corresponding to the lowest-lying state on the initial well, $\text{Tr}\{\hat{\rho}_t \hat{\rho}_0\}$, and traces with the Heaviside function to obtain the population on

the right side, $P_R = \text{Tr}\{\hat{\rho}_t\Theta(x; x_0)\}$ or traces with the complement of the Heaviside function to obtain the population on the left, $P_L = \text{Tr}\{\hat{\rho}_t(1 - \Theta(x; x_0))\}$. Finally, we look at the eigenvalues obtained by exact diagonalization of the Lindbladian to assess the principal modes/mechanisms of population transfer as well as the long-time final equilibrium state. We focus on the maximum amplitude non-zero real eigenvalue, to compute the decay time defined as follows:

$$T_X = -[\Re\lambda]^{-1} \tag{41}$$

which represents the slower decaying timescale of the Lindbladian. Note that this gives qualitative insight into the relaxation rate, while bypassing the more expensive requirement of performing dynamics propagation.

Simulating barrier crossing dynamics on a Kerr-Cat device

Barrier crossing dynamics of the type typically observed in chemical systems requires coupling the reaction coordinate to a bath of non-reactive DOFs which acts both as an energy source for activating the chemical system from the bottom of the reactant well to the vicinity of the barrier top and as an energy sink for stabilizing the system in the product well once barrier crossing occurred. Since the Kerr-Cat Hamiltonian in Eq. (15) only describes the dynamics along the reaction coordinate, treating it as a closed quantum system undergoing unitary dynamics would not generate the desirable chemical dynamics. Coupling the reaction coordinate to a thermal bath of nonreactive DOFs takes us to the domain of *nonunitary* open quantum systems dynamics. In what follows, we will assume that this dynamics is described by the following Lindblad quantum master equation:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}_{\text{KC}}, \hat{\rho}(t)] \quad (42)$$

$$+ \kappa (1 + n_{\text{th}}) \left[\hat{a} \hat{\rho}(t) \hat{a}^\dagger - \frac{1}{2} \{ \hat{a}^\dagger \hat{a}, \hat{\rho}(t) \} \right] \quad (43)$$

$$+ \kappa n_{\text{th}} \left[\hat{a}^\dagger \hat{\rho}(t) \hat{a} - \frac{1}{2} \{ \hat{a} \hat{a}^\dagger, \hat{\rho}(t) \} \right] \\ \equiv \mathcal{L} \hat{\rho}(t). \quad (44)$$

$$(45)$$

Here, $\hat{\rho}(t)$ is the density operator that describes the state of the reactive system, \hat{H}_{KC} is the Kerr-Cat Hamiltonian of the reactive system [Eq. (15)], $\{\kappa n_{\text{th}}, \kappa(n_{\text{th}} + 1)\}$ are parameters that determine the rates of bath-induced uphill and downhill transitions, respectively, and thereby the coupling strength between the reaction coordinate and the bath of non-reactive DOFs and \mathcal{L} is the Lindbladian superoperator.

Simulating the dissipative dynamics described by Eq. (45) was accomplished by vec-

torizing the density operator and matricizing the Lindbladian superoperator, followed by diagonalizing \mathcal{L} and propagating the vectorized density operator according to

$$\hat{\rho}(t) = e^{\mathcal{L}t} \hat{\rho}(0) \quad . \quad (46)$$

The initial state was chosen so that it is localized in the reactant well. To this end, we picked the first eigenstate of the Kerr-Cat Hamiltonian with more than 50% probability of being in the reactant well and then multiplied it by a sigmoidal function that filtered out the part of the wave function that resides in the product well. Given this reactant-well-localized wave function, $|\psi_R\rangle$, the initial density operator is given by $\hat{\rho}(0) = |\psi_R\rangle\langle\psi_R|$ (a pure state).

The barrier crossing rate constant is given by $k = 1/T_X$, where T_X defines the barrier crossing time scale. T_X was determined in two ways:

1. As the inverse of the real value of the smallest singular value of the Lindbladian supermatrix, obtained via diagonalization, as in figure 8a.
2. As the time scale of decay of $Tr[\hat{\rho}_t \Theta_X]$, obtained via fitting to an exponential, as in figure 8 (b).

The two methods for determining T_X gave similar results and found to exhibit the same behavior when it comes to the dependence of T_X on the Kerr-Cat parameters. The results reported in the text were obtained via method 1 unless otherwise noted (figure 8b).

The following analysis is for the case of $\Delta = 0$, and using the convention $\hbar = 1$ and K as a unit of energy. A complete description of the methodology is included in Computational Methods.

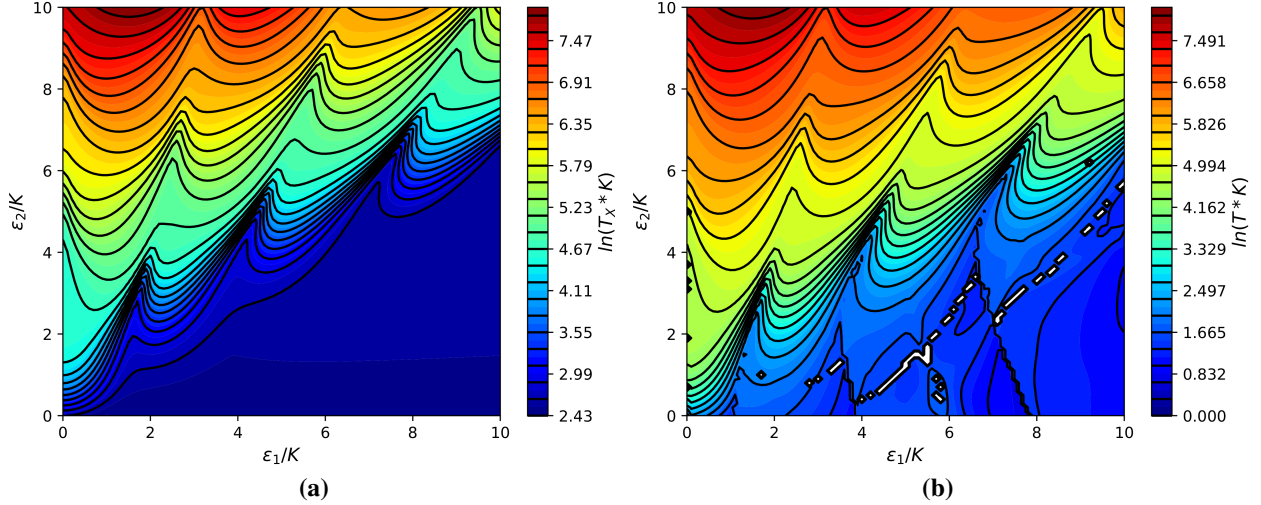


Figure 8: Relaxation timescales associated with the (a) Lindbladian maximal real eigenvalue (left) and (b) the dynamical relaxation rates (right) obtained by fitting the population traces as a function of the Kerr-Cat parameters ε_1 and ε_2 . Both plots use dissipation parameters $\kappa = 0.1$, $n_{\text{th}} = 0.1$.

The dependence of T_X on the Kerr-Cat parameters ε_1 and ε_2 is shown in Fig. 8. The plot shows a rich structure including (a) a zone in the lower right corner where the barrier crossing is very fast, which corresponds to a low barrier or a complete lack of a barrier, (b) Fast barrier crossing in the upper left corner for particular values of $(\varepsilon_1, \varepsilon_2)$ where the energy levels in the reactant and product wells are in resonance (see white lines in Figs. 8 and SI), and (c) alternation between "broad" and "thin" resonance transitions both as a function of ε_1 for fixed ε_2 and along the $(\varepsilon_1, \varepsilon_2)$ resonance line.

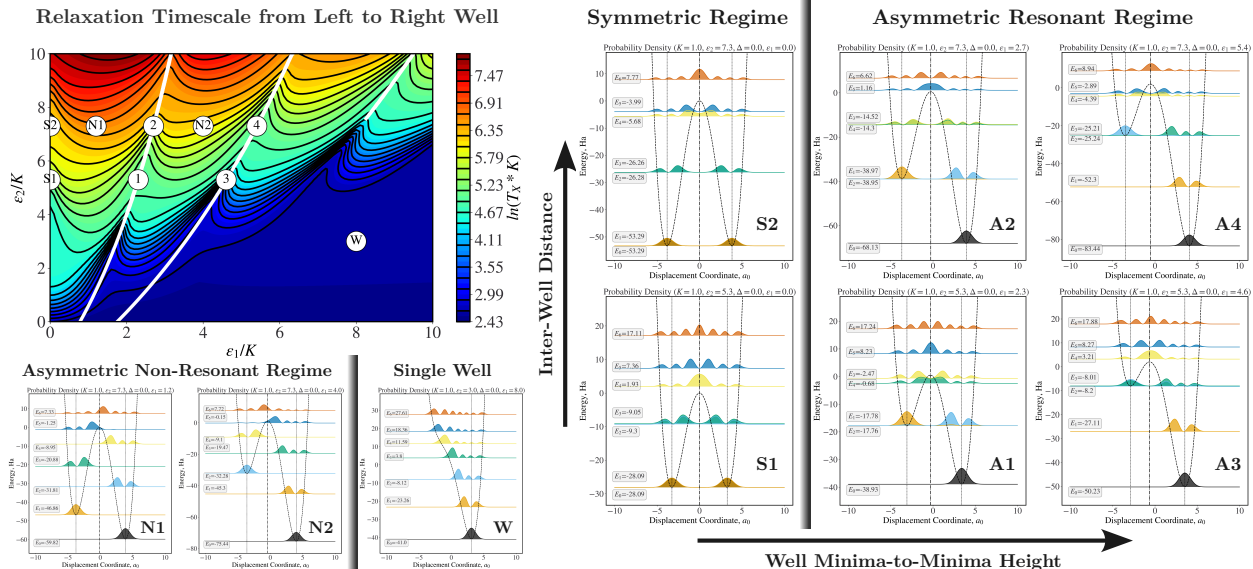


Figure 9: Resonant and non-resonant regimes of the eigendensities between both sides of the double-well along the $p = 0$ metapotential cut. Each state are plotted as a function of position superimposed on the metapotential cut spanning $x \in [-10, 10]$ Bohr. The vertical axis denotes the absolute energy obtained by diagonalizing the Hamiltonian. Panels include the asymmetric non-resonant regime (N1, N2), a region where the double-well description is no longer valid (W). The resonant regime falls along the white lines and reflect regimes with no asymmetry (S1, S2) as well as regions of increasing well asymmetry (A1-A2, A3-A4) by changing the minima-to-minima height.

The fast barrier crossing regimes correspond to resonances between the energy levels in the reactant and product wells which lead to efficient tunneling through the barrier. The aforementioned "thin" regions correspond to eigenstate overlap close the top of the barrier as well as a high state density at the barrier top, providing a transient state to retain population before decaying to the global ground state (see figure 8 and corresponding panels S1, 2, 3 of figure 9). By contrast the "broad" regimes contain degenerate states but no density centered at the top of the barrier, thus reducing the overall population transfer rate (see figure 8 and corresponding panels S2, 1, 4 of figure 9). However, the rate is nonetheless enhanced due to the presence of quasi-degenerate states near the barrier top, providing a pathway for barrier crossing. Furthermore, the intermediate states without resonant states have longer lifetimes due to lack of overlap between eigenstates or localized state density on either side of the well (see figure 8 and corresponding panels N1 and N2 of figure 9). Going along each of the

resonance lines showcases an increasing number of degenerate pairs of states with increasing ϵ_2 (figure 8: S1-S2; 1-2; 3-4). Going between different resonance lines with increasing ϵ_1 changes the first state index in resonance between the two wells (S1: first and second, 1: second and third, 3: third and fourth).

Finally, a decrease in the minimum-to-minimum height decreases the barrier height until the double-well is destroyed (figure 9, W). This decreases the relaxation lifetime as the kinetics driving the process is merely vertical de-excitation to the ground state. Although there can be a relaxation timescale associated with the process this is not a measurement of the kinetics of population transfer between the wells, as this is an ill-defined process in this parameter regime.

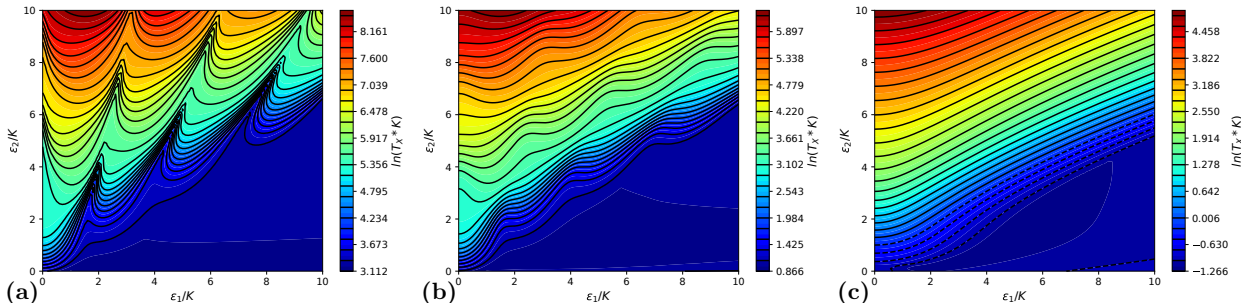


Figure 10: Dependence of timescale obtained by exact Lindbladian diagonalization on the dissipation parameter κ , for $n_{\text{th}} = 0.1$. (a) $\kappa = 0.05$. (b) $\kappa = 0.5$. (c) $\kappa = 5.0$.

Fig. 10 shows how the dependence of T_X on ϵ_1 and ϵ_2 is impacted by the the strength of coupling between the reaction coordinate and the bath of nonreactive DOFs, as measured by κ . As expected, T_x shows an overall trend of increasing with decreasing coupling strength, which can be traced back to the fact that the rate of activation from the bottom of the reactant well to to the vicinity of the barrier top and stabilization in the product well after barrier crossing are determined by κ . Additionally, the dependence of T_X on ϵ_1 and ϵ_2 is seen to become less structured with increasing κ , which can be traced back to ability of dissipation to wash out resonance effects. More specifically, while tunnelling dominates the kinetics at low values of κ , classical-like barrier crossing and thereby TST/Arrhenius-like kinetics is observed at larger values of κ . A more extensive set of data that showcases this

observation for a wider range of parameter regimes is provided in the supporting information.

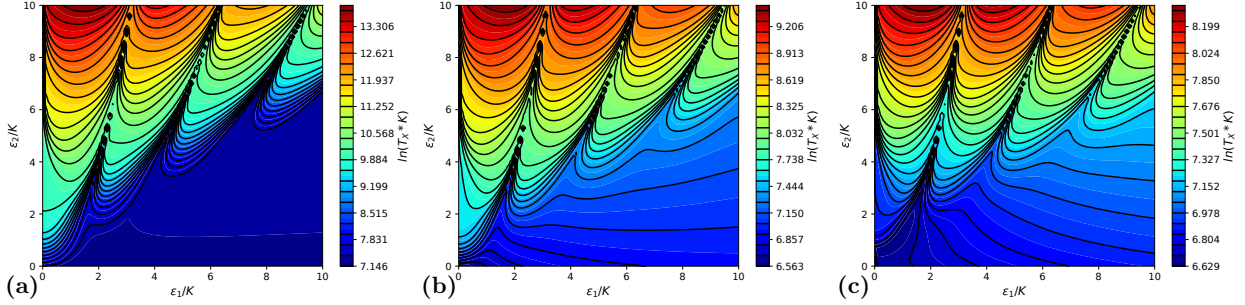


Figure 11: Dependence of timescale obtained by exact Lindbladian diagonalization on the dissipation parameter κ , for $\kappa = 0.001$. (a) $n_{th} = 0.05$. (b) $n_{th} = 0.5$. (c) $n_{th} = 1.0$.

Finally, Fig. 11 shows how the dependence of T_X on ϵ_1 and ϵ_2 is impacted by the bath temperature, as measured by n_{th} . While T_X shows an overall increase with decreasing n_{th} , the structure is seen to be minimally impacted by changing n_{th} .

Basis Set Convergence

In this section, we explore the convergence of the Kerr-Cat Hamiltonian parameters to the number of Eigen-basis used. In Fig. 12, we present the timescales obtained from the exact diagonalization of the Lindbladian as a function of Hamiltonian parameters ϵ_1 and ϵ_2 , for a different number of Eigen-basis. As can be appreciated, with $n_{basis} > 10$ the timescales are semi-quantitative converged, and with $n_{basis} > 20$ quantitative agreement is found. Unless otherwise stated, we used $n_{basis} = 20$ for the device dynamics.

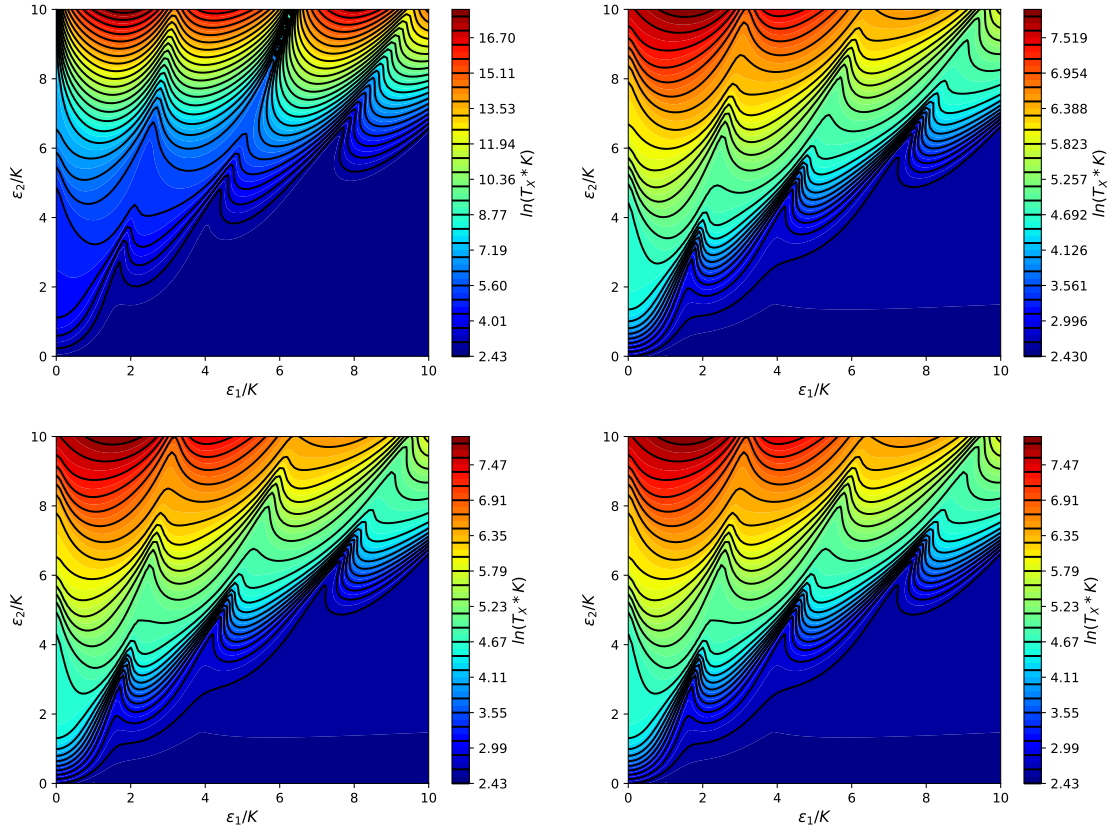


Figure 12: Convergence of Lindbladian eigenvalue timescale as a function of the number of Eigen-basis. (a) $n_{basis} = 5$. (b) $n_{basis} = 10$. (c) $n_{basis} = 20$. (d) $n_{basis} = 30$.

Chemical Potentials

The chemical potentials were obtained from the literature, and are listed within the tables in this section.

Table 3: Literature chemical potential parameters given by expression $V_{\text{literature}} = k_1x - k_2x^2 - k_3x^3 + k_4x^4$

System	k_4	k_3	k_2	k_1	Units
Thymine-Adenine (DNA) ³⁷	0.02068986	0.00525515	0.0413797	0.0157655	E_h
Malonaldehyde (cis-trans) ^{39,40}	0.00009374	0.000109	0.00299	0.005232	a.u.
Malonaldehyde (cis-cis) ^{39,40}	0.000714286	0	0.004	0	a.u.

Table 4: Literature chemical potential parameters given by expression $V_{\text{literature}} = V_1\{\exp(-2a_1[x - r_1]) - 2\exp[-a_1(x - r_1)]\} + V_2\{\exp(2a_2[x - r_2]) - 2\exp[a_2(x - r_2)]\}$

System	V_1	V_2	a_1	a_2	r_1	r_2	Units
Guanine-Cytosine (DNA) ³⁸	0.1617	0.082	0.305	0.755	-2.7	2.1	a.u.

Furthermore, we note that the adenine-thymine potential is expressed in terms of a unitless length parameter $\zeta = x/x_0$, which has been estimated to be $x_0 = 1.9592 a_0$ based on matching the energy eigenvalues listed in reference 37. For the dynamics shown in this work, the given literature potentials were fit to the simpler double-well potential, without a cubic polynomial term,

$$\hat{V}_{\text{DW}} = k_4\hat{x}^4 + k_2\hat{x}^2 + k_1\hat{x}_1 \tag{47}$$

Dynamics Trajectories and Rate Fits

This section lists additional trajectory plots for both the double-well and Kerr-Cat analog for different values of c and a plot of the resulting fitted rates. These plots cover the dissipation parameters listed in the main text.

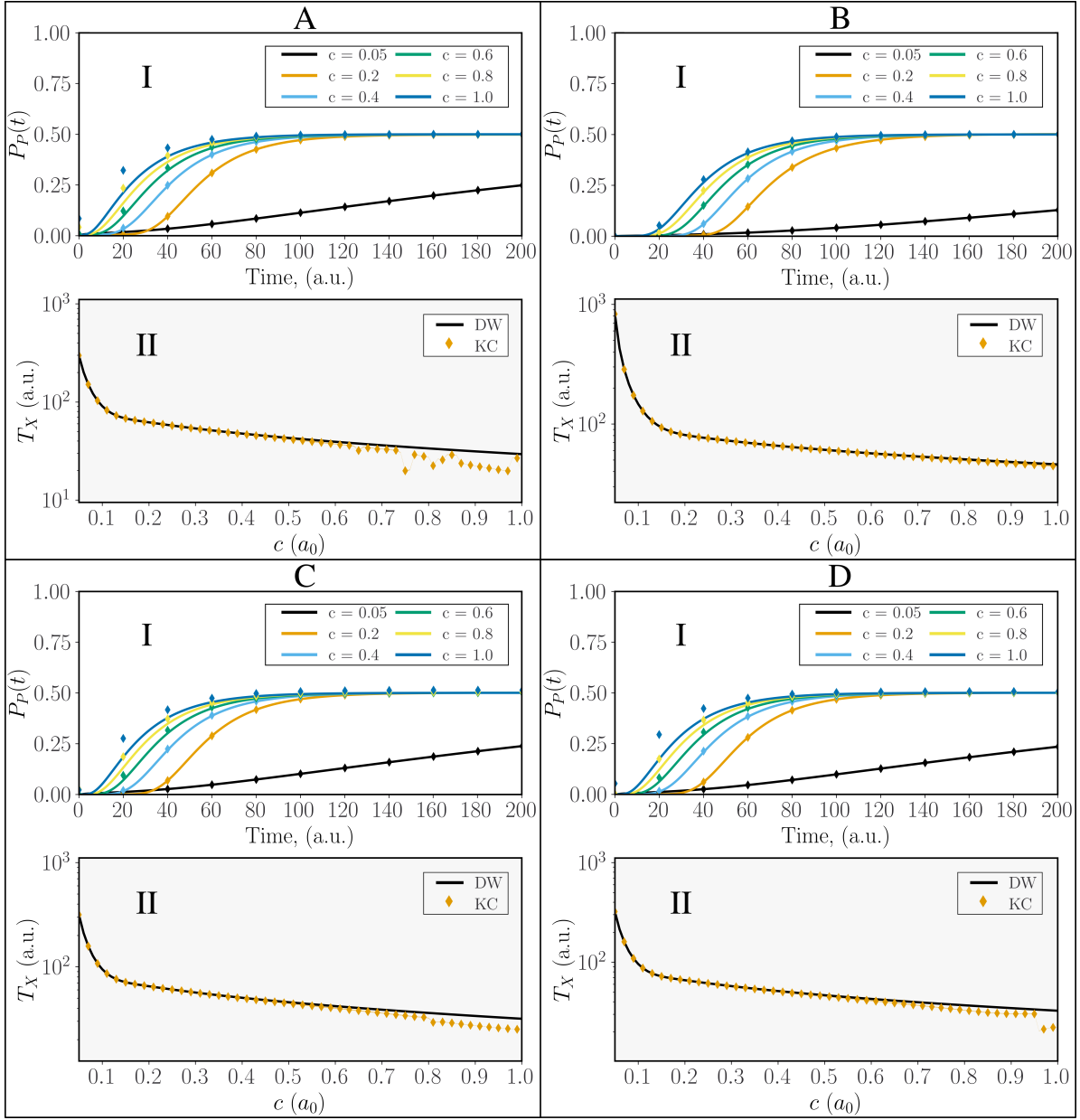


Figure 13: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.1$, and $n_{\text{th}} = 0.1$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels.

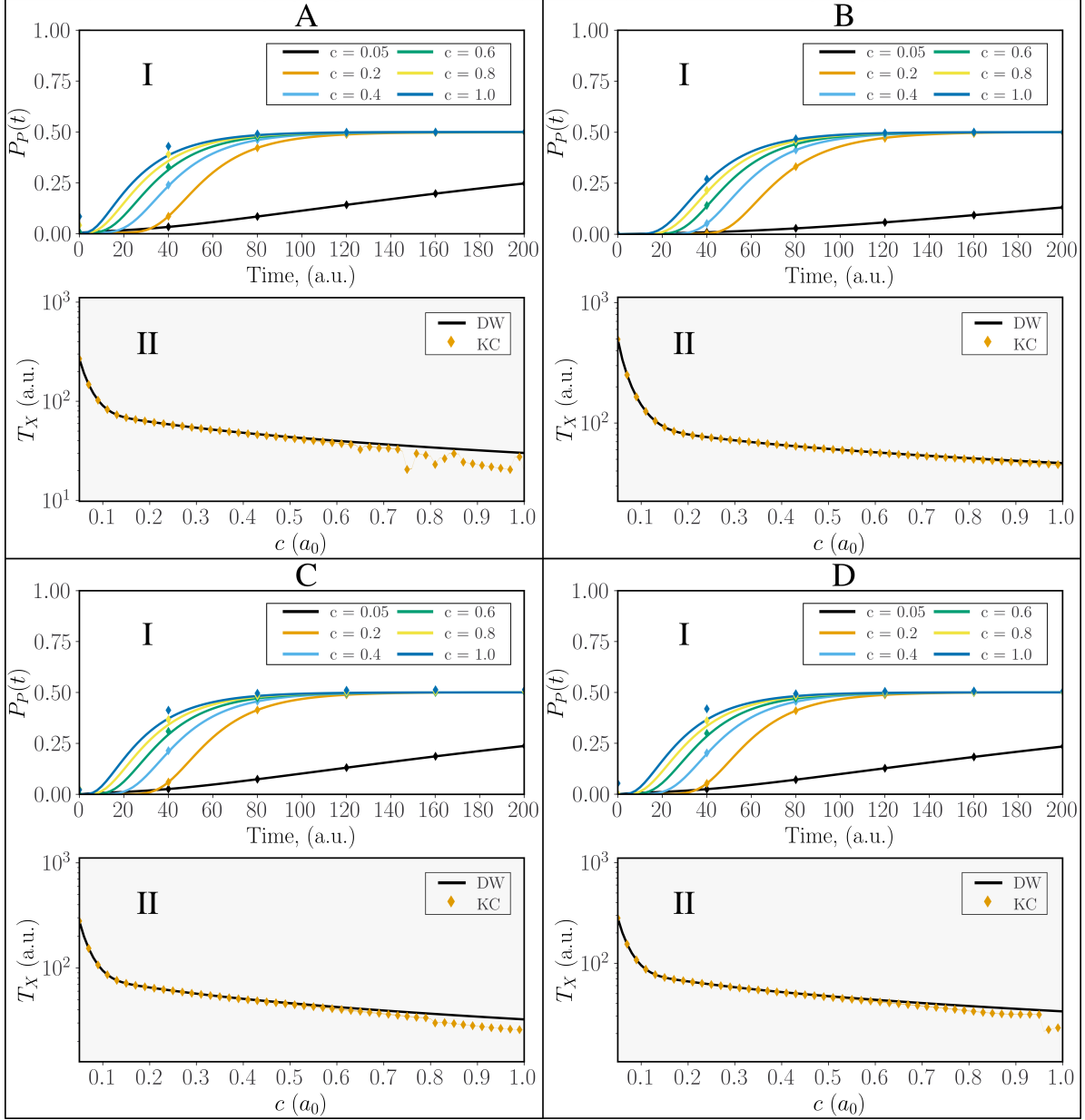


Figure 14: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.1$, and $n_{th} = 0.05$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels.

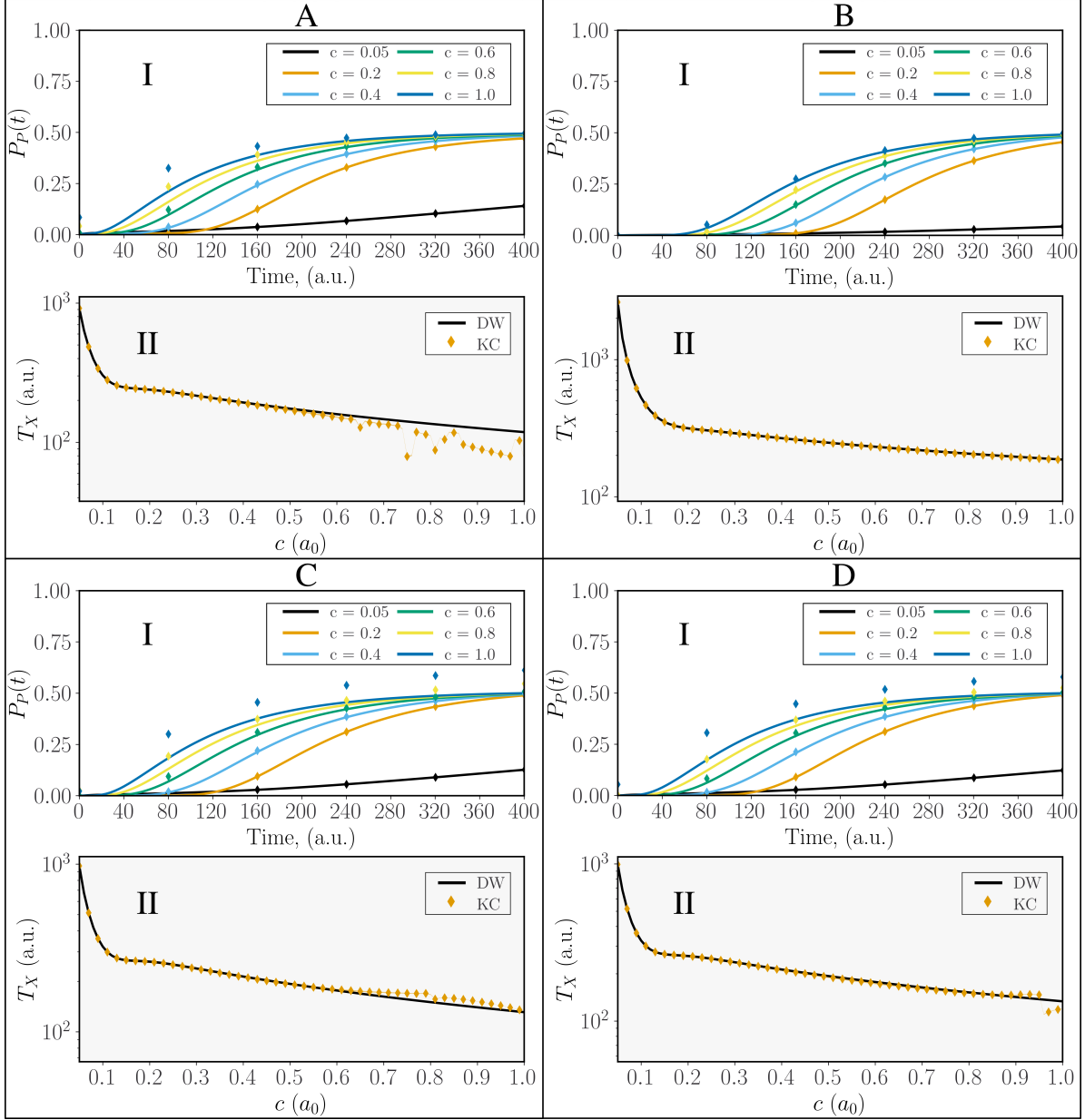


Figure 15: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.025$, and $n_{th} = 0.1$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels.

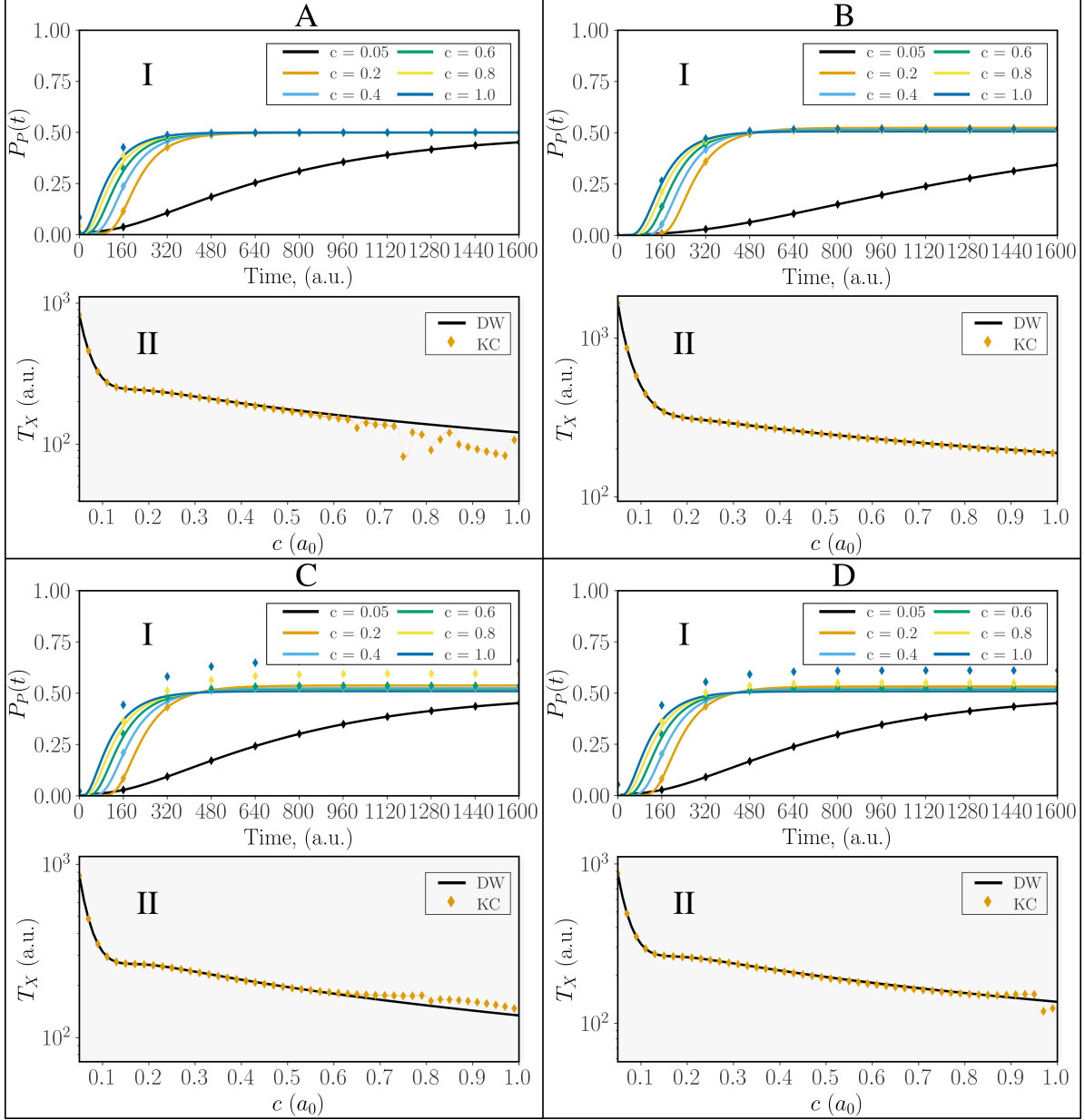


Figure 16: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.025$, and $n_{th} = 0.05$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels.

Basis Benchmark for Dynamical Evolution

This section showcases the dynamics evolution figures for the four systems, using a different number of basis set to showcase the convergence of the results listed in the main text. The figures showcase the results of using a Fock space of dimension 50, 100 and 150 to accurately represent the Hamiltonian and eigenstates, which are then used for the dynamics propagation in a reduced subspace. For all cases, 50 eigenstates were used for the dynamics propagation, which incorporate many levels beyond the barrier top energy. For some of the listed systems, dynamics convergence with respect to number of eigenstates is observed for values much smaller than than fifty. Deviations of the Kerr-Cat fitted rates at larger c -values, result from the Hamiltonian perturbative terms that are sensitive to the value of c and errors associated with the fitting protocol.

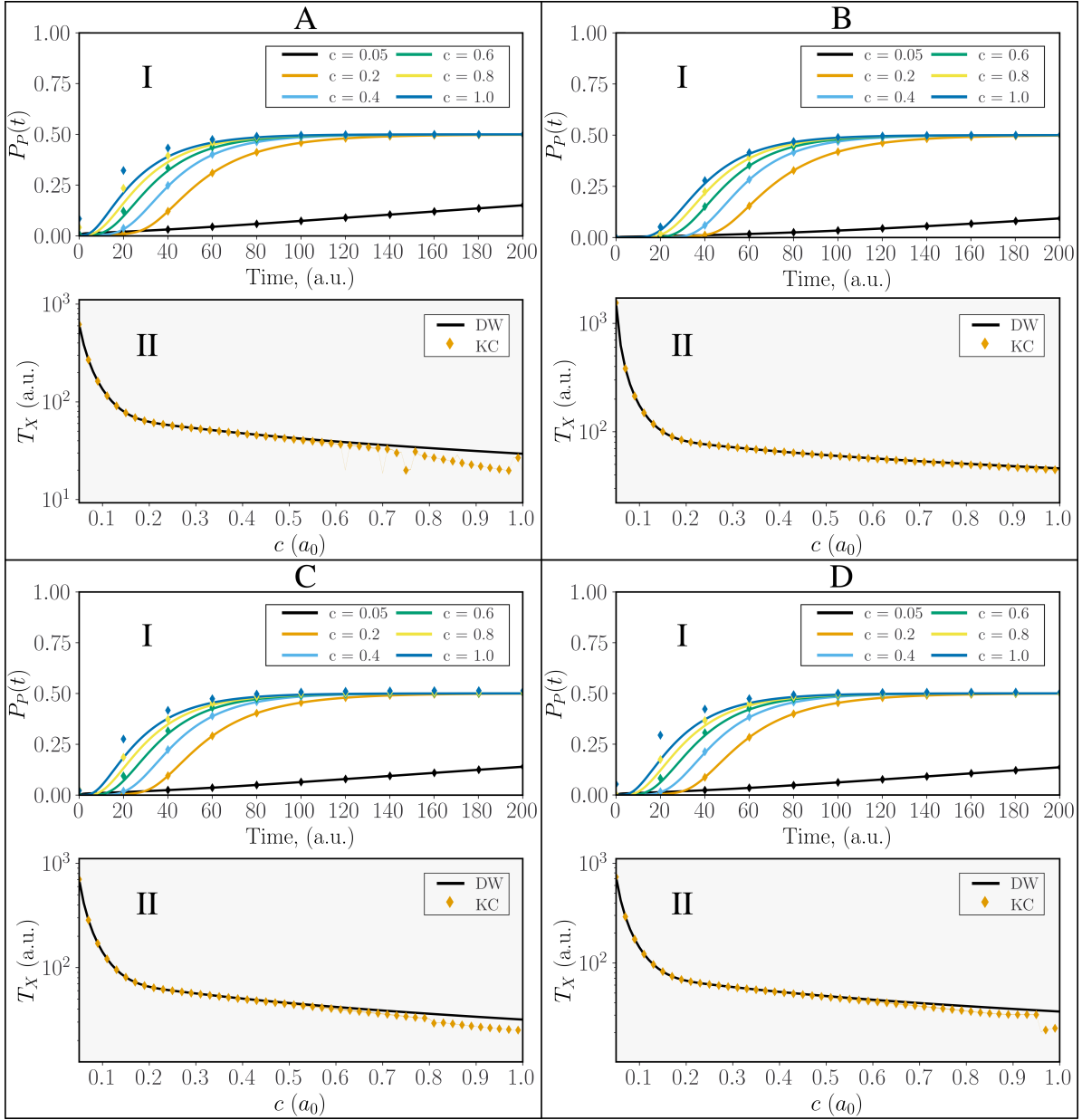


Figure 17: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.1$, and $n_{\text{th}} = 0.1$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels. These results were generated using 50 Fock basis for Hamiltonian and initial state preparation and a subspace of 50 eigenfunctions for dynamics propagation.

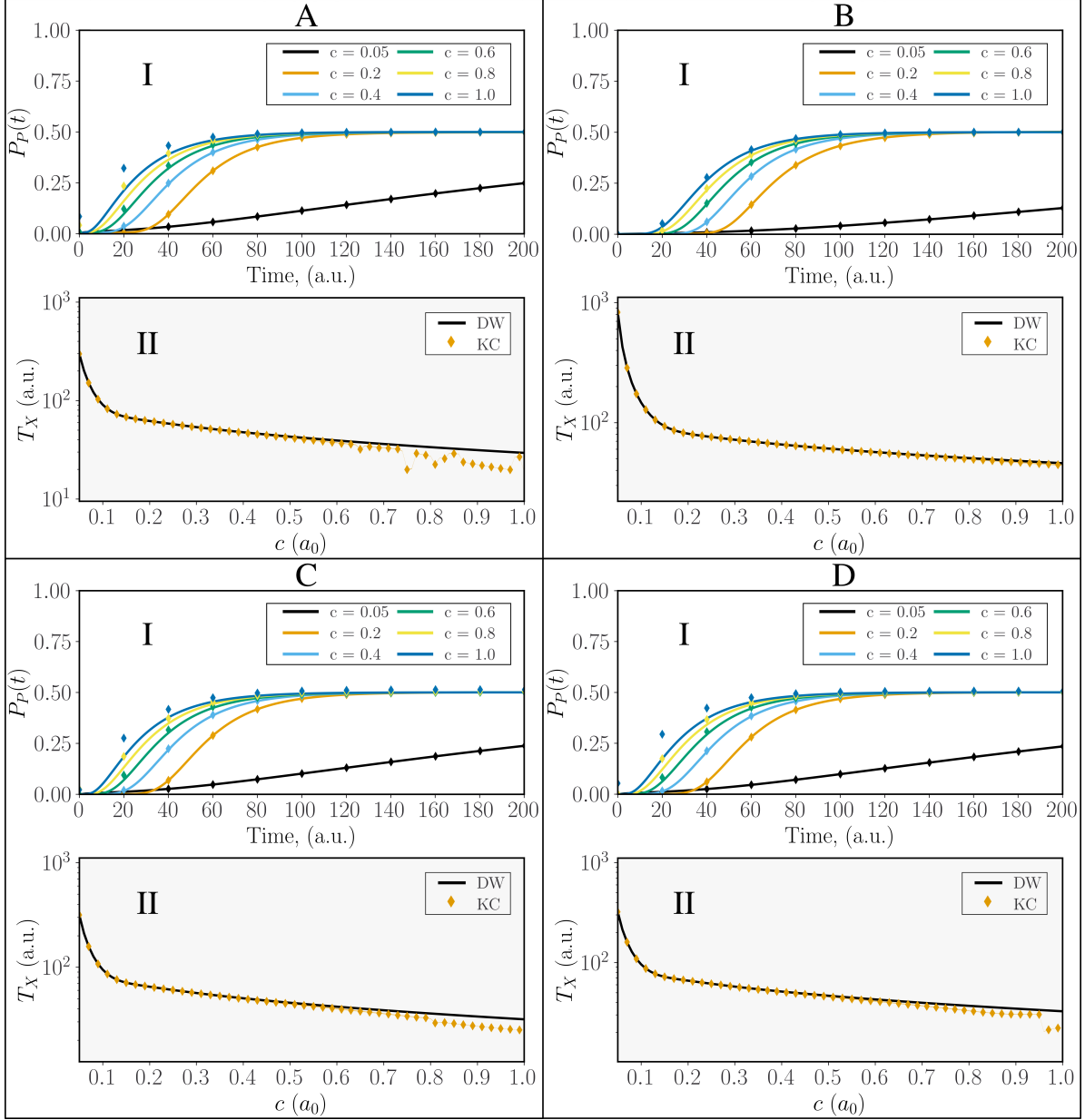


Figure 18: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.1$, and $n_{th} = 0.1$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels. These results were generated using 100 Fock basis for Hamiltonian and initial state preparation and a subspace of 50 eigenfunctions for dynamics propagation.

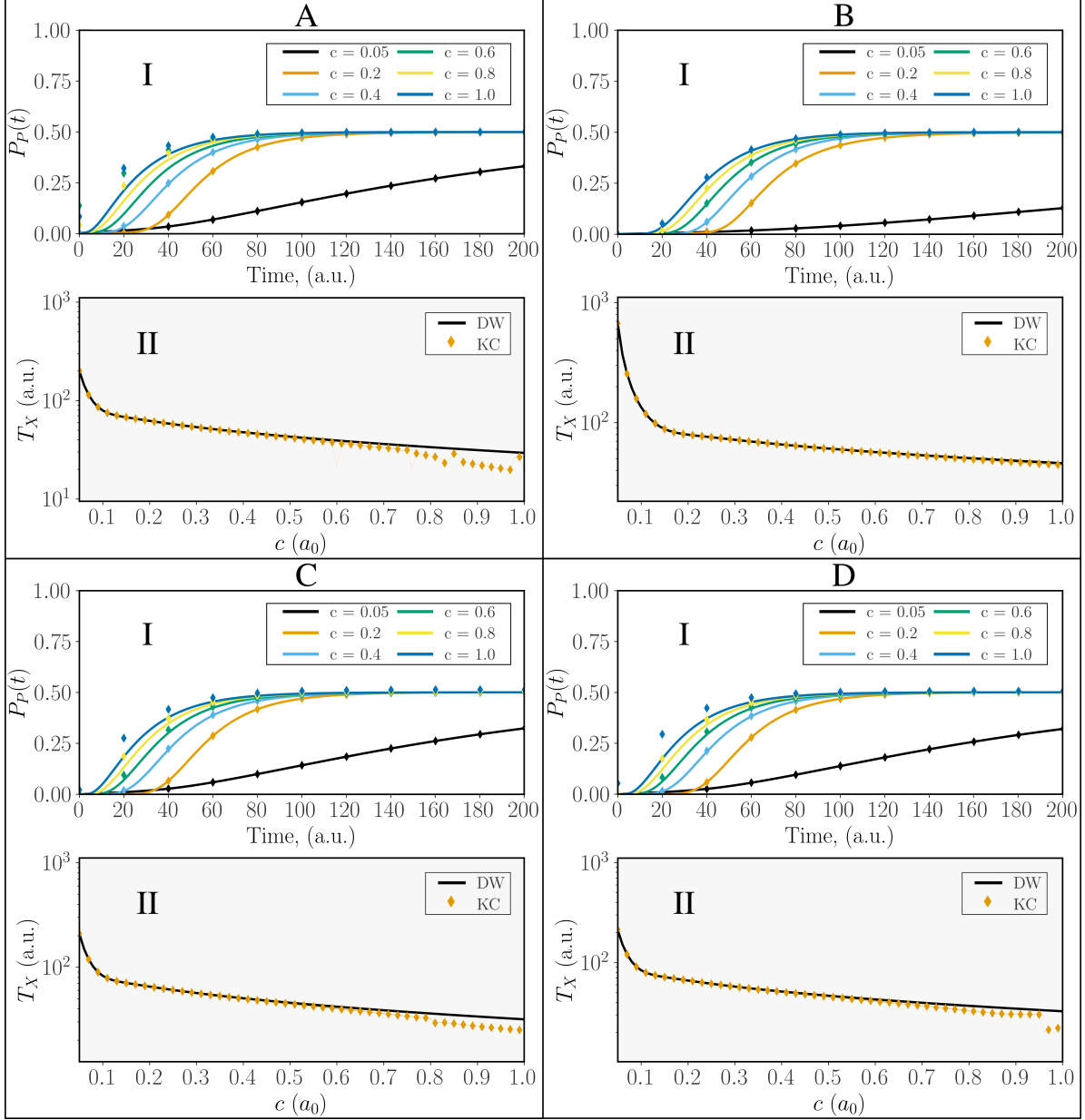


Figure 19: Comparison of observables computed obtained with \hat{H}_{DW} (solid lines) and \hat{H}_{KC} (diamonds) as a function of c , using $\kappa = 0.1$, and $n_{th} = 0.1$. The time evolution of the product population for the four proton transfer reactions are shown in the top subpanels. The corresponding inverse reaction rate constants are shown in the bottom subpanels. These results were generated using 150 Fock basis for Hamiltonian and initial state preparation and a subspace of 50 eigenfunctions for dynamics propagation.