

Supplementary Information: Critical Chemical Equivalence: The SymC Principle Governing Catalysis and Reactivity

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1 Exceptional Point Mathematics

At the critical damping boundary $\chi = 1$, the system exhibits an exceptional point (EP)—a non-Hermitian degeneracy where eigenvalues and eigenvectors coalesce simultaneously. This section develops the mathematical structure and physical consequences.

1.1 Green’s Function Kernel Transition

The response function $G(t)$ governs how the system reacts to perturbations. For the damped oscillator, the Green’s function exhibits qualitatively different forms depending on χ :

Underdamped regime ($\chi < 1$):

$$G(t) = \frac{1}{\omega_d} e^{-\Gamma t/2} \sin(\omega_d t), \quad \omega_d = \Omega \sqrt{1 - \chi^2} \quad (1)$$

The response oscillates with damped frequency $\omega_d < \Omega$. Energy initially deposited into the coordinate rings back and forth before dissipating.

Critically damped regime ($\chi = 1$):

$$G(t) = t e^{-\Omega t} \quad (2)$$

The polynomial prefactor t signals the defective nature of the EP. The system relaxes monotonically with maximum efficiency—no oscillation, no sluggishness.

Overdamped regime ($\chi > 1$):

$$G(t) = \frac{1}{2\gamma}(e^{-\lambda_-t} - e^{-\lambda_+t}), \quad \lambda_{\pm} = \Omega(\chi \pm \sqrt{\chi^2 - 1}) \quad (3)$$

Two distinct exponential decays with separate timescales. The slower mode dominates long-time behavior, leading to kinetic trapping.

1.2 Eigenvector Coalescence

At $\chi = 1$, the geometric multiplicity of the repeated eigenvalue $\lambda = -\Omega$ drops from 2 to 1. The Jordan normal form requires a generalized eigenvector:

$$(A - \lambda I)\mathbf{v}_1 = 0, \quad (A - \lambda I)\mathbf{v}_2 = \mathbf{v}_1 \quad (4)$$

The general solution becomes:

$$\mathbf{x}(t) = e^{-\Omega t}[(c_1 + c_2 t)\mathbf{v}_1 + c_2 \mathbf{v}_2] \quad (5)$$

This structure is universal to all second-order systems at critical damping, explaining why $\chi = 1$ represents a fundamental boundary independent of microscopic details.

1.3 Chemical Significance

The exceptional point at $\chi = 1$ marks where:

- Oscillatory character transforms into translational motion
- Energy storage transitions to energy dissipation
- Reversible dynamics become irreversible
- Information about initial conditions is erased optimally

For chemical reactions, crossing $\chi = 1$ along the reaction coordinate represents the commitment point: the system transitions from potentially reversible to irreversibly committed to product formation.

2 χ -Preserving Coarse Graining

2.1 Standard Coarse Graining Failures

Traditional coarse-graining methods eliminate degrees of freedom based on:

- **Energy hierarchy:** Remove high-energy modes first

- **Timescale separation:** Average over fast modes, integrate out slow modes
- **Entropy production:** Retain modes with largest dissipation

None of these criteria distinguish between dynamically persistent and transient modes. A high-energy underdamped mode ($\chi \ll 1$) stores energy without dissipating; a low-energy overdamped mode ($\chi \gg 1$) dissipates without progressing. Standard methods miss this distinction.

2.2 The χ -Selection Rule

For a system with coupled modes $\{q_k\}$ characterized by $\{\Omega_k, \Gamma_k\}$, compute:

$$\chi_k = \frac{\Gamma_k}{2\Omega_k} \quad (6)$$

Partition modes by χ value:

1. **Persistent sector** ($0.8 \leq \chi_k \leq 1.2$): Retain as explicit dynamical variables
2. **Noise sector** ($\chi_k < 0.8$): Average over as stochastic forcing
3. **Constraint sector** ($\chi_k > 1.2$): Eliminate as quasi-static boundary conditions

The effective reaction coordinate inherits:

$$\chi_{\text{eff}} = \frac{\sum_{k \in \text{persistent}} |c_k|^2 \Gamma_k}{2\sqrt{\sum_{k \in \text{persistent}} |c_k|^2 \Omega_k^2}} \quad (7)$$

where c_k are coupling coefficients determined by the full Hamiltonian.

2.3 Comparison to Mori-Zwanzig Theory

Mori-Zwanzig formalism derives exact generalized Langevin equations:

$$\ddot{Q}(t) + \int_0^t K(t-s) \dot{Q}(s) ds + \Omega^2 Q(t) = F(t) \quad (8)$$

The memory kernel $K(t)$ encodes bath effects. Standard MZ projections preserve energy conservation and detailed balance but do not preserve χ . The χ -coarse graining approach selects projections that maintain near-critical operation, sacrificing formal exactness for dynamical relevance.

2.4 Substrate Inheritance

If substrate components satisfy $\chi_i \approx 1$, the composite system inherits:

$$\chi_{\text{composite}} \approx 1 \quad (9)$$

This explains why:

- Enzyme active sites constructed from critically damped residue motions operate near $\chi = 1$
- Catalysts with d-bands near the Fermi level (broad linewidth, $\chi \approx 1$) create critically damped adsorbate dynamics
- Optimal solvents for electron transfer have relaxation times matching substrate oscillation periods

Stability propagates through organizational levels via χ -inheritance.

3 Zusman Solvent-Controlled Electron Transfer

3.1 Derivation of the Solvent-Controlled Regime

Zusman's theory considers diabatic electronic states $|D^+A^- \rangle$ and $|DA \rangle$ coupled by V , with nuclear coordinate Q representing solvent polarization. The coupled equations are:

$$\begin{pmatrix} \dot{P}_1 \\ \dot{P}_2 \end{pmatrix} = \begin{pmatrix} -k_1 - iV/\hbar & iV/\hbar \\ iV/\hbar & -k_2 - iV/\hbar \end{pmatrix} \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} \quad (10)$$

where $k_{1,2}$ are solvent relaxation rates.

In the high-friction limit ($k_1, k_2 \gg V/\hbar$), populations equilibrate faster than electronic coupling can induce coherent transfer. The rate becomes:

$$k_{\text{ET}} = \frac{1}{\tau_L} \frac{1}{1 + \tau_L \omega_0} \quad (11)$$

where $\tau_L = (k_1 + k_2)^{-1}$ is the longitudinal relaxation time and $\omega_0 = 2V/\hbar$.

3.2 Adiabaticity Parameter

Define the dimensionless parameter:

$$g = \frac{2\pi V^2 \tau_L}{\hbar \sqrt{4\pi \lambda k_B T}} \quad (12)$$

Adiabatic regime ($g \gg 1$): Electronic coupling is strong relative to nuclear motion. The rate reduces to:

$$k_{\text{ET}} \approx \frac{1}{\tau_L} \quad (13)$$

independent of V . This is the solvent-controlled limit.

Nonadiabatic regime ($g \ll 1$): Standard Marcus theory applies:

$$k_{\text{ET}} = \frac{2\pi}{\hbar} V^2 \sqrt{\frac{1}{4\pi \lambda k_B T}} \exp \left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_B T} \right) \quad (14)$$

3.3 Connection to χ Framework

The Zusman parameter g relates directly to χ via:

$$g \sim \frac{V^2 \tau_L}{\lambda} \sim \frac{\Gamma}{\Omega} \quad (15)$$

The solvent-controlled regime ($g > 1$) corresponds to $\chi > 1$ (overdamped), where friction dominates. The rate $k_{\text{ET}} \sim 1/\tau_L$ is the high-friction limit of Kramers theory applied to electron transfer.

Both Kramers and Zusman independently arrive at the same turnover behavior: rates maximize when friction and frequency are comparable, precisely the $\chi \approx 1$ condition.

4 Detailed χ Estimation: TEMPO in Propylene Carbonate

4.1 Parameter Collection

For the TEMPO $^\bullet$ /TEMPO $^+$ system in propylene carbonate:

- Reorganization energy: $\lambda \approx 0.7$ eV (typical for nitroxide radicals)
- Longitudinal relaxation time: $\tau_L \approx 1.2$ ps
- Effective spring constant: $k \approx \lambda/\Delta Q^2$ where $\Delta Q \approx 0.5$ Å (solvent shell reorganization)
- Effective mass: $m \approx 10$ amu (collective solvent coordinate)

4.2 Calculation

Angular frequency:

$$\Omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{2\lambda}{m\Delta Q^2}} \approx 2 \times 10^{13} \text{ rad/s} \quad (16)$$

Damping rate:

$$\Gamma \approx \frac{1}{\tau_L} \approx 8 \times 10^{11} \text{ s}^{-1} \quad (17)$$

Stability ratio:

$$\chi = \frac{\Gamma}{2\Omega} \approx \frac{8 \times 10^{11}}{4 \times 10^{13}} \approx 0.02 \quad (18)$$

4.3 Interpretation

This simple single-mode estimate suggests TEMPO in propylene carbonate operates in a moderately underdamped regime. The observed $1/\tau_L$ scaling indicates movement *toward* the solvent-controlled limit as friction increases across the solvent series.

Important caveats:

- The effective mass m is highly uncertain; doubling m cuts χ in half
- Multi-mode coupling increases effective Γ
- Non-Markovian memory effects broaden the effective linewidth
- These estimates provide order-of-magnitude guidance, not precise predictions

For acetonitrile ($\tau_L \approx 0.2$ ps), the same calculation gives $\chi \approx 0.1$, confirming the trend toward higher χ with increased friction.

5 Relation to Transition State Theory

5.1 TST Assumptions

Transition state theory rests on three assumptions:

1. Quasi-equilibrium between reactants and transition state
2. Boltzmann distribution over configurations
3. No recrossing: trajectories passing through TS proceed to products

The rate is:

$$k_{\text{TST}} = \frac{k_B T}{h} e^{-\Delta G^\ddagger / (k_B T)} \quad (19)$$

TST works well when barrier crossing is fast compared to equilibration. It provides a thermodynamic upper bound on rates.

5.2 χ as Dynamical Correction

The χ framework extends TST by identifying when the no-recrossing assumption fails:

$\chi < 1$ at the transition state: The system oscillates near the barrier. Trajectories may cross multiple times before committing to products. TST overestimates the rate; a transmission coefficient $\kappa < 1$ is required.

$\chi \approx 1$ at the transition state: No-recrossing holds; TST is accurate. The system exhibits fastest monotonic relaxation away from the barrier.

$\chi > 1$ at the transition state: Barrier crossing is diffusion-limited. The system spends excessive time in the transition region. TST remains valid but sluggish kinetics result from overdamped dynamics.

5.3 Grote-Hynes Friction Correction

Grote-Hynes theory generalizes TST to include friction effects:

$$k_{\text{GH}} = \kappa_{\text{GH}} k_{\text{TST}}, \quad \kappa_{\text{GH}} = \frac{\lambda_r}{\omega_b} \quad (20)$$

where λ_r is the reactive mode frequency corrected for friction.

This transmission coefficient can be expressed in terms of χ :

$$\kappa_{\text{GH}} = -\chi + \sqrt{\chi^2 + 1} \quad (21)$$

Grote-Hynes reduces to Kramers in appropriate limits and exhibits the same turnover behavior at $\chi \approx 1$.

5.4 When TST Fails

TST cannot predict:

- Which systems exhibit back-transfer versus completion
- Why structurally similar compounds show different yields
- The dynamical origin of BEP violations in catalysis
- The transition between adiabatic and nonadiabatic electron transfer

The χ framework addresses these gaps by adding dynamical selection criteria complementary to TST’s thermodynamic baseline.

6 Limitations and Domain of Validity

6.1 Linearity Assumption

The framework assumes dynamics linearizable near stationary points:

$$V(q) \approx V_0 + \frac{1}{2}kq^2 + \mathcal{O}(q^3) \quad (22)$$

Breakdown: Strongly anharmonic systems such as barrierless proton transfer in very floppy hydrogen-bond networks may require extensions. For such systems, frequency-dependent $\Omega(q)$ and $\Gamma(q)$ must be considered.

Resolution: Local $\chi(q)$ can be defined along the reaction path, with the framework predicting that efficient reactions maintain $\chi(q) \approx 1$ throughout the transformation.

6.2 Markovian Friction

The damping term $\Gamma\dot{q}$ assumes memoryless friction. This holds when bath correlation times are short compared to system dynamics.

Breakdown: Electron transfer in structured protein environments exhibits non-Markovian effects due to slow conformational gating. The effective friction becomes frequency-dependent:

$$\Gamma \rightarrow \gamma(\omega) = \Gamma_0 \frac{\omega_c^2}{\omega^2 + \omega_c^2} \quad (23)$$

Resolution: Frequency-dependent $\chi(\omega)$ can be defined. Grote-Hynes theory provides the machinery for incorporating memory effects while preserving the $\chi \approx 1$ optimality condition.

6.3 Single Effective Coordinate

The framework treats reactions as evolving along a single effective coordinate $q(t)$. Real systems involve coupled multidimensional surfaces.

Breakdown: Multi-path reactions with competing mechanisms, deep quantum tunneling with interfering amplitudes, and strongly coupled vibrational modes may not reduce cleanly to a single χ value.

Resolution:

- For separable modes: Each mode has χ_k ; the reaction proceeds via modes with $\chi_k \approx 1$
- For nonseparable modes: Define χ_{eff} via weighted coupling (Section S2)
- For quantum interference: Extend to density matrix formalism with Lindblad damping

6.4 Classical versus Quantum

The oscillator model is fundamentally classical. Quantum effects include:

- Tunneling through barriers
- Zero-point energy corrections
- Quantum coherence between electronic states

Resolution: The χ framework extends to open quantum systems via Lindblad master equations. The dephasing rate γ_ϕ plays the role of classical damping Γ , and the SymC critical damping principle applies equally to quantum dissipative dynamics.

6.5 Scope Summary

The χ framework provides:

- **First-order organizing principle** for dynamical regime classification
- **Qualitative predictions** robust across systems and scales
- **Quantitative guidance** when parameters are well-characterized

It is not:

- A replacement for detailed quantum chemistry calculations
- The final word on all chemical dynamics
- A universal formula yielding exact rates for arbitrary systems

The power lies in identifying *when* and *why* chemical transformations succeed or fail based on a universal stability criterion.

7 Expanded Falsification Protocols

7.1 Electron Transfer: Detailed Tests

Test 1: Friction-Dependent Yield

Setup: Fixed donor-acceptor pair with known λ and ΔG° . Vary solvent viscosity by temperature or mixture composition.

Measurement: Transient absorption to quantify charge-separated state yield versus back-transfer yield.

Prediction: Yield maximum occurs at intermediate viscosity corresponding to $\chi \approx 1$. Too low: underdamped, back-transfer dominates. Too high: overdamped, slow initial transfer.

Falsification: If yield depends only on λ and ΔG° with no systematic friction dependence.

Test 2: Femtosecond Spectral Signatures

Setup: Pump-probe spectroscopy with sub-100 fs resolution. Track electronic state populations and coherences.

Measurement: Time-resolved absorption or emission spectra revealing wavepacket dynamics.

Prediction:

- $\chi < 1$: Oscillatory wavepacket motion, beat frequencies in populations
- $\chi \approx 1$: Spectral peak merging, extreme broadening without oscillation
- $\chi > 1$: Smooth monotonic decay, no coherent features

Falsification: If spectral evolution shows no qualitative transition near calculated $\chi = 1$.

7.2 PCET: Detailed Tests

Test 3: Pressure-Induced Mechanism Switching

Setup: PCET system with known stepwise pathway at ambient conditions. Apply hydrostatic pressure 0–10 kbar.

Measurement: Kinetic isotope effects, pH dependence, intermediate detection via stopped-flow or flash-quench.

Prediction: Transition from stepwise (detectable intermediates, pH-dependent, moderate KIE) to concerted (no intermediates, pH-independent, large KIE) occurs when calculated χ reaches 0.8–1.2.

Falsification: If mechanism switching is uncorrelated with χ or occurs at χ far from unity.

Test 4: Anomalous Isotope Effects

Setup: PCET reactions with H/D substitution. Measure KIEs across varying friction conditions.

Measurement: k_H/k_D as a function of solvent, temperature, pressure.

Prediction: KIE maximum when $\chi_H \approx 1$, because deuteration shifts χ_D out of the critical window due to mass change.

Falsification: If KIE shows no special behavior near $\chi = 1$ or follows standard semiclassical predictions independent of friction.

7.3 Catalysis: Detailed Tests

Test 5: Volcano Plot Outliers

Setup: Systematic DFT calculations of χ for adsorbates on catalyst surfaces. Compare with experimental activity data.

Measurement: Binding energies, vibrational frequencies, and linewidths from spectroscopy. Activity from turnover frequency measurements.

Prediction: Outliers below the volcano (optimal binding but low activity) have $\chi \ll 1$ or $\chi \gg 1$. High-activity outliers despite suboptimal binding have $\chi \approx 1$.

Falsification: If outlier activity correlates with binding energy alone, with no χ dependence.

Test 6: Isotope Effects in Catalysis

Setup: $^{14}\text{N}_2/^{15}\text{N}_2$ dissociation on Fe(111) and Fe(110) surfaces. In-situ IR to track vibrational shifts.

Measurement: Dissociation rate ratio k_{14}/k_{15} as a function of temperature and promoter coverage.

Prediction: Fe(111) ($\chi \approx 1$) shows anomalously large isotope effect because mass change shifts χ out of critical window. Fe(110) ($\chi \ll 1$) shows smaller effect consistent with standard kinetic theory.

Falsification: If isotope effects are identical across surfaces or follow standard predictions independent of χ .

Test 7: Linewidth-Activity Correlation

Setup: In-situ high-resolution IR spectroscopy during catalytic turnover. Vary catalyst composition, promoters, and temperature.

Measurement: Substrate vibrational linewidth $\Delta\nu$ and catalytic turnover frequency simultaneously.

Prediction: Activity maximizes at intermediate linewidth corresponding to $\chi = \Delta E/(2h\nu) \approx 1$. Too narrow: underdamped, unreactive. Too broad: overdamped, poisoned.

Falsification: If linewidth is uncorrelated with activity or maximum activity occurs at narrowest or broadest linewidths.

7.4 Cross-Domain Consistency

Test 8: Universal χ Window

Setup: Compile χ estimates from electron transfer (TEMPO series), PCET (ruthenium-tyrosine), and catalysis (N_2/Fe) at their respective optimal conditions.

Prediction: All optimal systems cluster within $\chi \in [0.8, 1.2]$ despite completely different chemistries.

Falsification: If optimal χ values are scattered randomly or show domain-specific clustering outside this range.

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