

Quantum Reaction Rates in Nonlinear Dissipative Systems

Oli Bridge

St Catharine's College

Part III Project
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Non-Adiabatic Effects in Metals

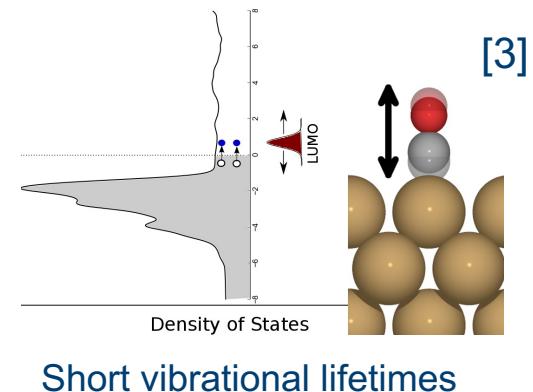
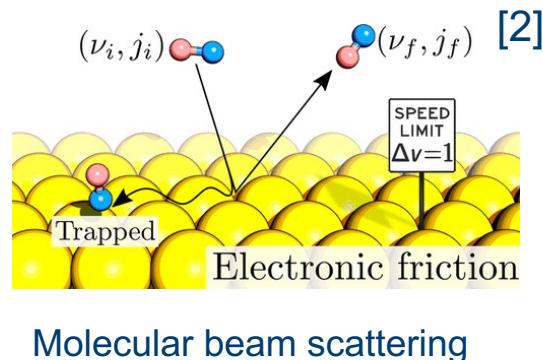
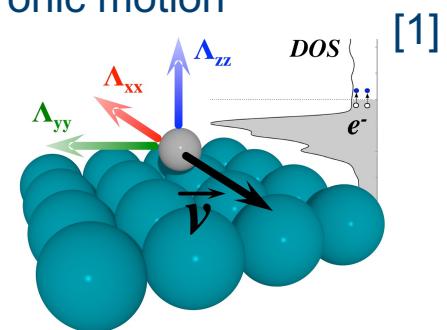
- Born-Oppenheimer approximation decouples nuclear and electronic motion

$$\hat{H}_{\text{tot}} = \hat{T}_{\text{nuc}} + \hat{H}_{\text{elec}}$$

$$\hat{H}_{\text{elec}}|\psi_{\text{elec}}(\mathbf{x}; \mathbf{X})\rangle = E_{\text{elec}}(\mathbf{X})|\psi_{\text{elec}}(\mathbf{x}; \mathbf{X})\rangle$$

$$(\hat{T}_{\text{nuc}} + E_{\text{elec}}(\mathbf{X}))|\psi_{\text{nuc}}(\mathbf{X})\rangle = E_{\text{tot}}|\psi_{\text{nuc}}(\mathbf{X})\rangle$$

- Breaks down for metallic systems due to non-adiabatic effects
- Metals have no band gap - low energy electronic excitations leads to ‘electronic friction’
- Position-dependent



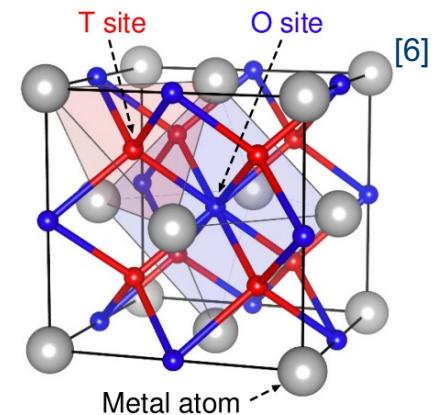
Condensed Phase Systems – Harmonic Bath

- Model of a system linearly coupled to a bath of harmonic oscillators^[4]

$$H(p, q, \mathbf{p}_b, \mathbf{x}) = \frac{p^2}{2\mu} + V(q) + \sum_{i=1}^{N_b} \left[\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 \left(x_i - \frac{c_i}{m_i\omega_i^2}q \right)^2 \right]$$

Linear coupling

- To capture a position-dependent friction, we would require nonlinear coupling
- This has been studied classically for model potentials^[5] – affects the recrossing dynamics
- We are interested in the motion of light atoms
- Nuclear quantum effects (NQEs) are important for such systems



Condensed Phase Systems – NQEs

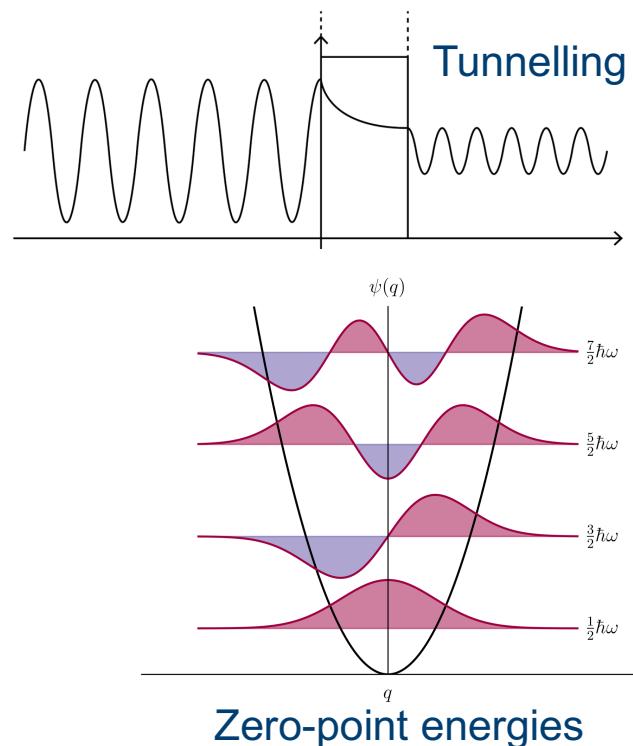
- Computational study of condensed phase systems has been a popular area of research
- Molecular dynamics simulations fail to capture NQEs
- Rapid decoherence in the condensed phase
- Quantum statistics + classical dynamics



PIMD – Path integral molecular dynamics^[7]



RPMD – Ring polymer molecular dynamics^[8]



Project Aims

- Develop a system-bath model under the influence of nonlinear coupling
- Investigate the effects on the rate when accounting for NQEs (RPMD)
- Apply this to the electronic friction problem for the rate of hydrogen hopping in palladium

Talk Outline

- Methods: RPMD rates and nonlinear system-bath model
- Results: Position-dependent friction for a model double-well potential
- Results: Position-dependent friction for hydrogen hopping in Pd

RPMD Rate Theory

- RPMD Hamiltonian as an extended classical phase space

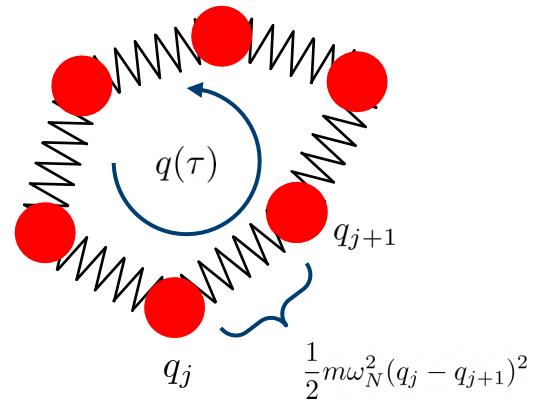
$$H_N(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^N \left[\frac{p_j^2}{2m} + \frac{1}{2}m\omega_N^2(q_j - q_{j+1})^2 + V(q_j) \right]$$

- RPMD rate constant from the flux-side TCF

$$k^{(N)}(T) = \frac{1}{Q_r^{(N)}(T)} \lim_{t \rightarrow \infty} \tilde{C}_{fs}^{(N)}(t)$$



$$k^{(N)}(T) = \lim_{t \rightarrow \infty} \frac{\langle \delta(q^\ddagger - \bar{q})(\bar{p}/m)h(\bar{q}(t) - q^\ddagger) \rangle}{\langle h(q^\ddagger - \bar{q}) \rangle}$$



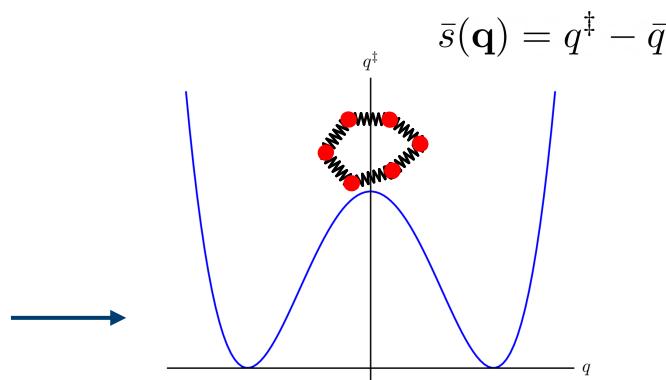
RPMD Rate Theory – Bennett Chandler Method [9]

- Rate constant can be factorised into a dynamic term and a free energy term [10]

$$k^{(N)}(T) = \kappa(t_p) k^{\text{QTST}}(T)$$

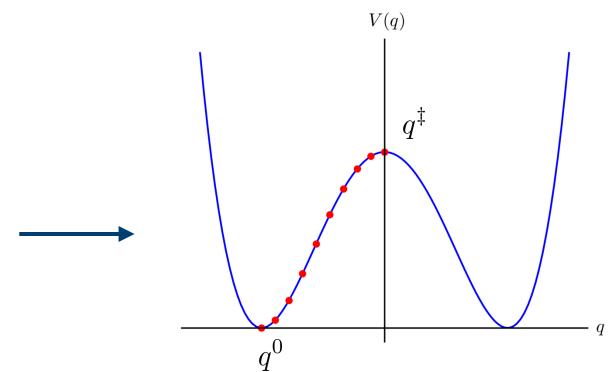
- Transmission coefficient

$$\kappa(t) = \frac{\langle \delta(q^\ddagger - \bar{q})(\bar{p}/m) h(\bar{q}(t) - q^\ddagger) \rangle}{\langle \delta(q^\ddagger - \bar{q})(\bar{p}/m) h(\bar{p}) \rangle}$$



- QTST rate from thermodynamic integration

$$k^{\text{QTST}}(T) = \frac{1}{(2\pi\beta m)^{1/2}} \frac{\langle \delta(q' - \bar{q}) \rangle}{\langle h(q^\ddagger - \bar{q}) \rangle} \exp \left(-\beta \int_{q^0}^{q^\ddagger} dq' \frac{d\mathcal{F}(q')}{dq'} \right)$$



Nonlinear System-Bath – Theory

- System-Bath Hamiltonian for nonlinear coupling

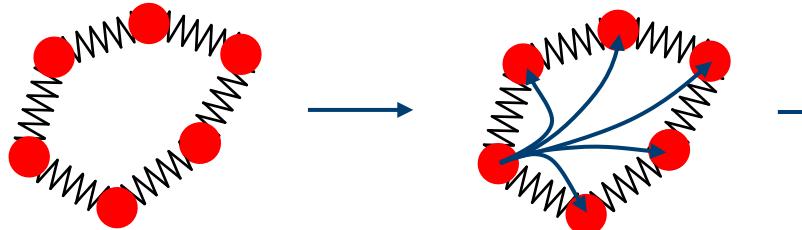
$$H(p, q, \mathbf{p}_b, \mathbf{x}) = \frac{p^2}{2\mu} + V(q) + \sum_{i=1}^{N_b} \left[\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 \left(x_i - \frac{f_i(q)}{m_i\omega_i^2} \right)^2 \right]$$

General function

- Separable coupling approximation – frequency dependence is the same for all positions

$$f_i(q) = c_i g(q)$$

- Bath renormalization potential couples the fluctuation modes together



$$\mathcal{F} = \frac{1}{\beta} \ln Z_N^{\text{bath}} + \frac{1}{\beta} \sum_{k=0}^{N-1} \ln \left(\beta_N \hbar \sqrt{\omega^2 + \omega_k^2 + \frac{\tilde{\eta}(\omega_k)}{m} \omega_k} \right)$$

- Friction makes RP more classical – lower free energy c.f. harmonic ZPE?
- No! RP free energy *increases* with friction for a harmonic potential

Nonlinear System-Bath – Model

- DW1 double well potential

$$V(q) = -\frac{1}{2}m\omega_b^2 q^2 + \frac{m^2\omega_b^4}{16V_0^\ddagger}q^4$$

$$\begin{aligned}m &= m_p \\ \omega_b &= 500 \text{ cm}^{-1} \\ V_0^\ddagger &= 2085 \text{ cm}^{-1}\end{aligned}$$

- Ohmic spectral density with exponential cut-off

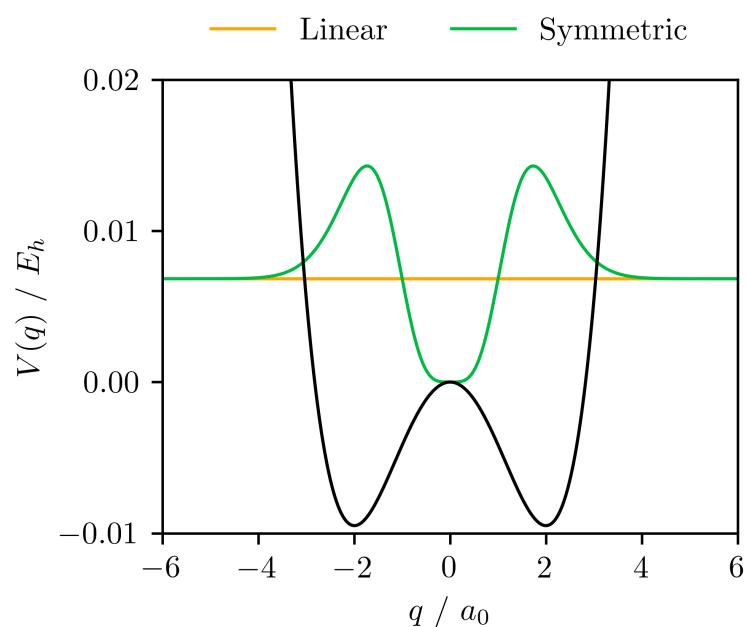
$$J(q, \omega) = \eta_0(q) \omega e^{-\omega/\omega_c}$$

$$\begin{aligned}\omega_c &= 500 \text{ cm}^{-1} \\ \eta_0(q) &= \left(\frac{\partial g(q)}{\partial q} \right)^2\end{aligned}$$

- Two friction regimes: ‘linear’ and ‘symmetric’ friction

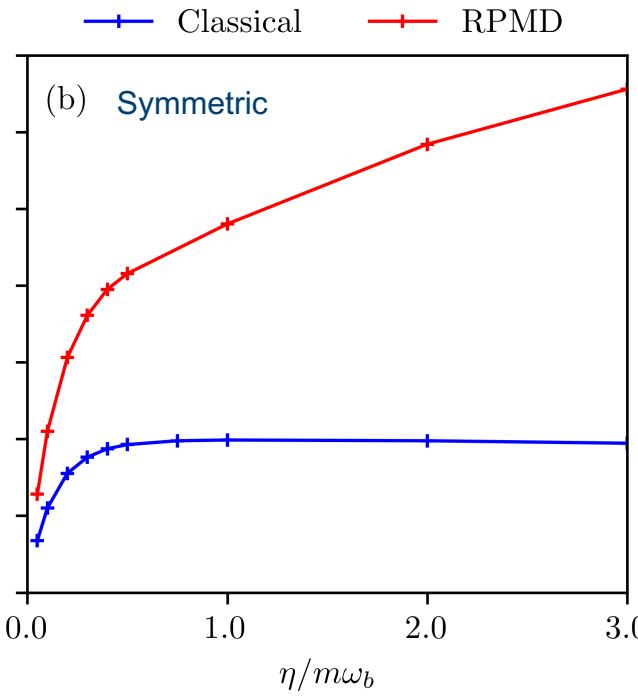
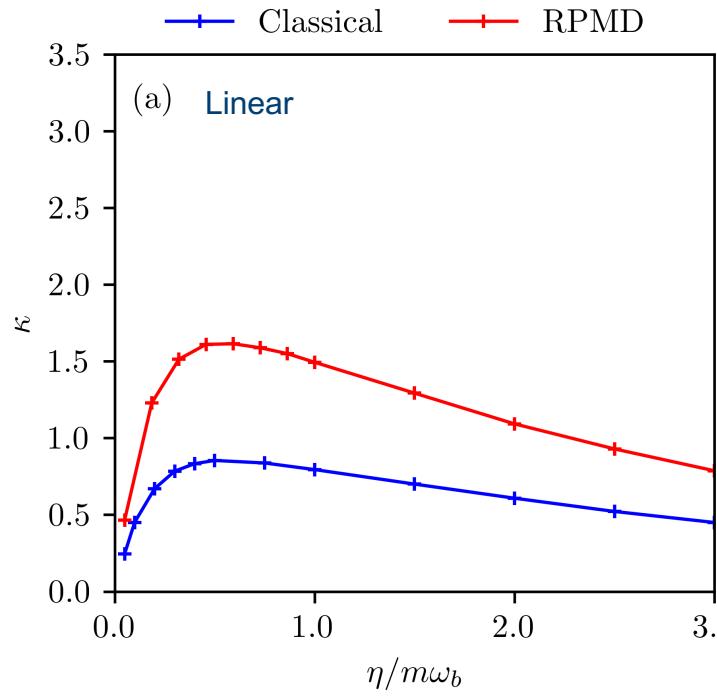
Position-independent

Position-dependent

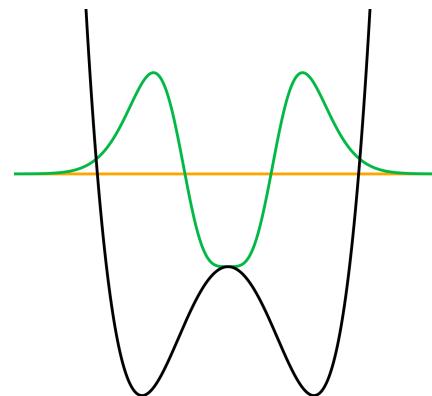


Nonlinear System-Bath – 300K Results

- DW1 double well potential for T = 300K; rate vs bath friction
- Dimensionless rate has been normalized by classical TST $\longrightarrow \kappa = \frac{k^{(N)}(T)}{k_{\text{cl}}^{\text{TST}}(T)}$

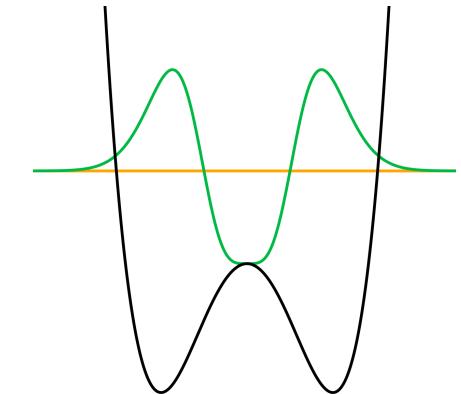
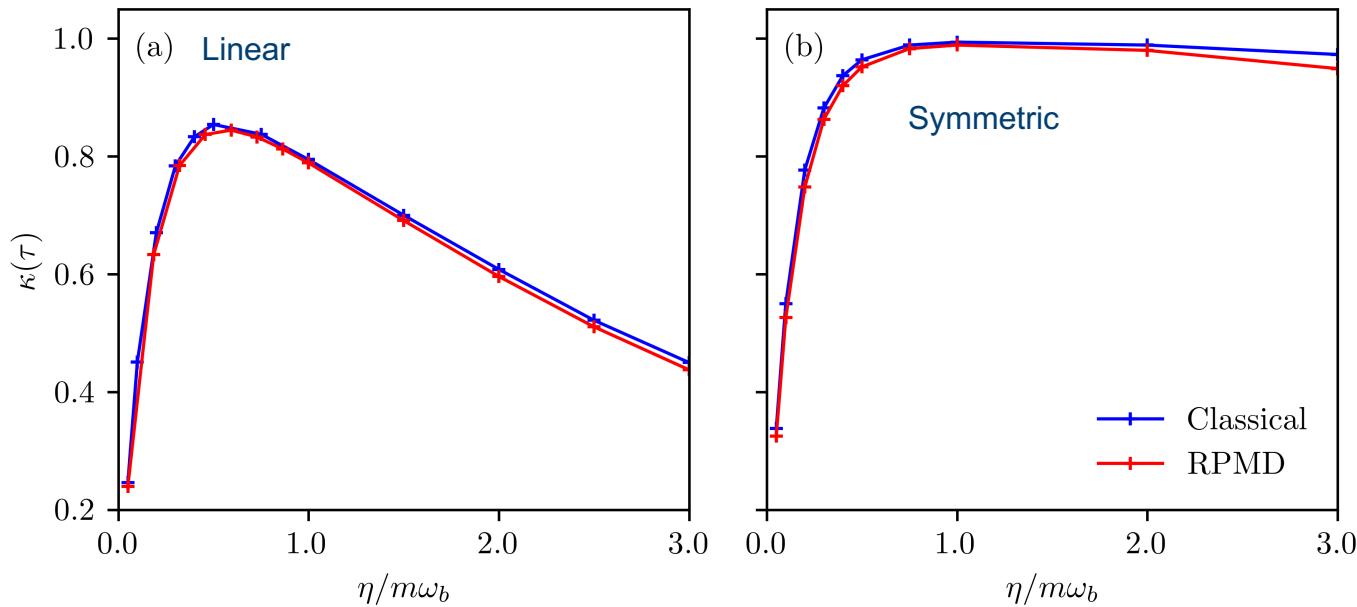


$$\kappa = \frac{k^{(N)}(T)}{k_{\text{cl}}^{\text{TST}}(T)}$$



Nonlinear System-Bath – 300K Results

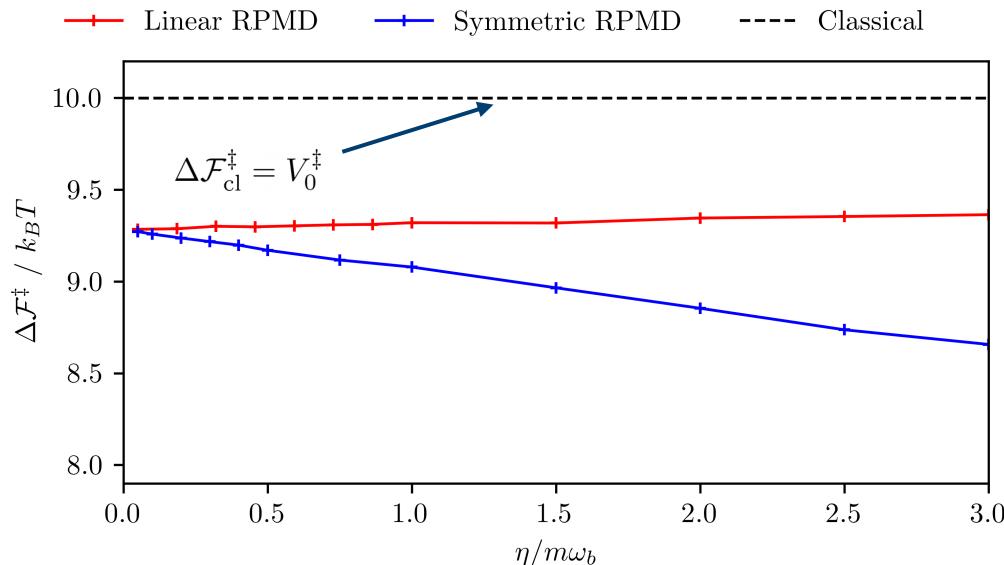
Transmission factors, 300K



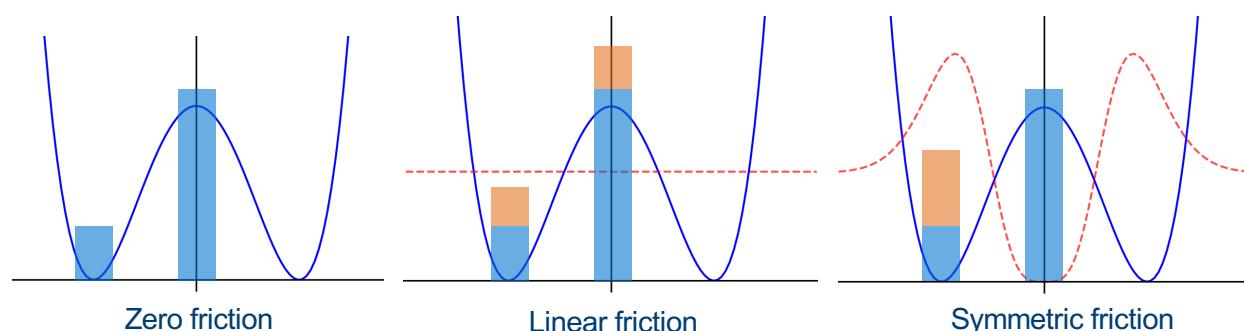
- Symmetric friction limits recrossing
- Ring polymer dynamics are behaving classically

Nonlinear System-Bath – 300K Results

Free energy barriers, 300K



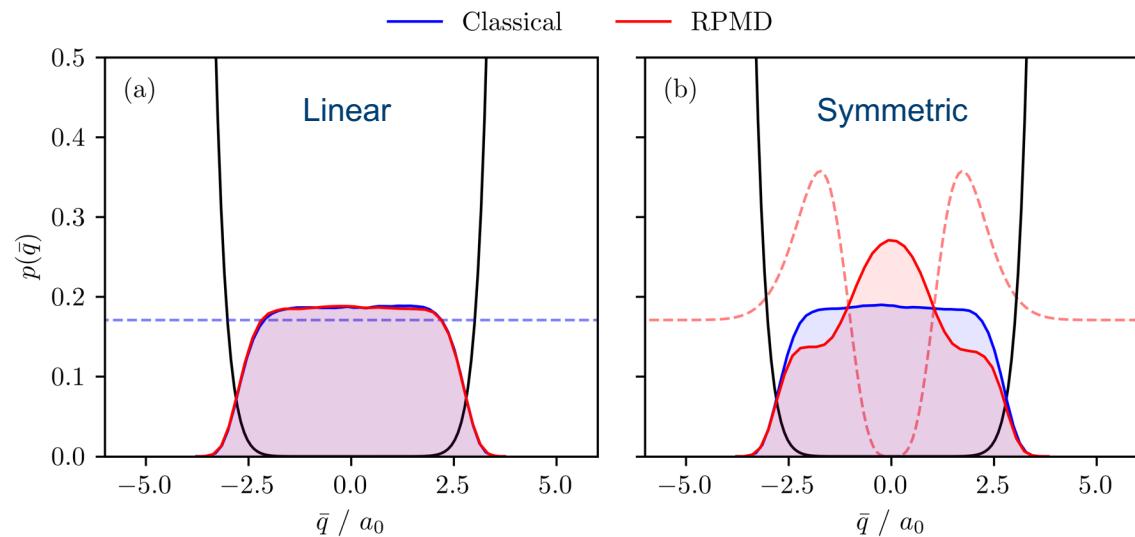
- Free energy is contributing to the rate increase
- Classical free energy barrier is unaffected by friction
- Increasing friction raises the free energy for quantum system



Nonlinear System-Bath – 300K Results

- This can be shown by the centroid position distributions in a ‘box-like’ potential

$$V(q) = aq^{12}$$



- Friction-driven localisation is a nuclear quantum effect
- Consistent with distorted instanton paths^[11]

Hydrogen Hopping in Pd – Model

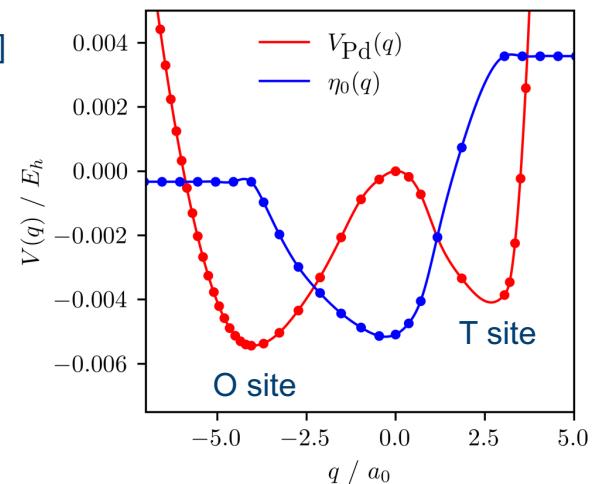
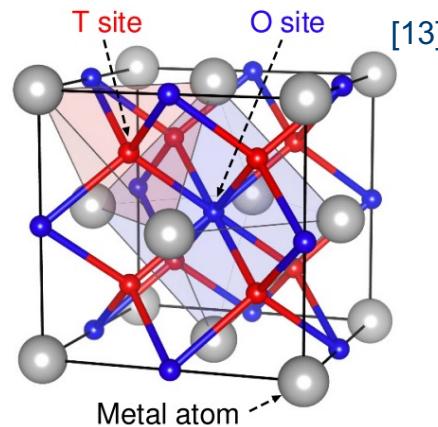
- Spectral density determined from ab initio calculation of the friction tensor

$$J_{ij}(\mathbf{q}, \omega) = \pi \hbar \sum_{\nu, \nu'} \langle \psi_\nu | \partial_i \psi_{\nu'} \rangle \langle \psi_{\nu'} | \partial_j \psi_\nu \rangle \omega^2 (f(\epsilon_\nu) - f(\epsilon_{\nu'})) \delta(\omega - \Omega_{\nu, \nu'})$$

$\Omega_{\nu, \nu'} = (\epsilon_{\nu'} - \epsilon_\nu)/\hbar$

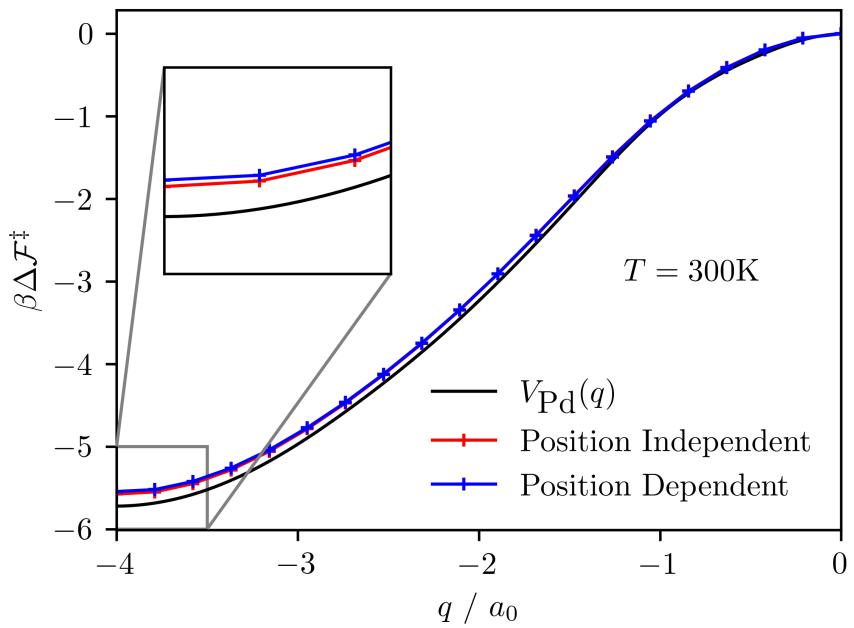
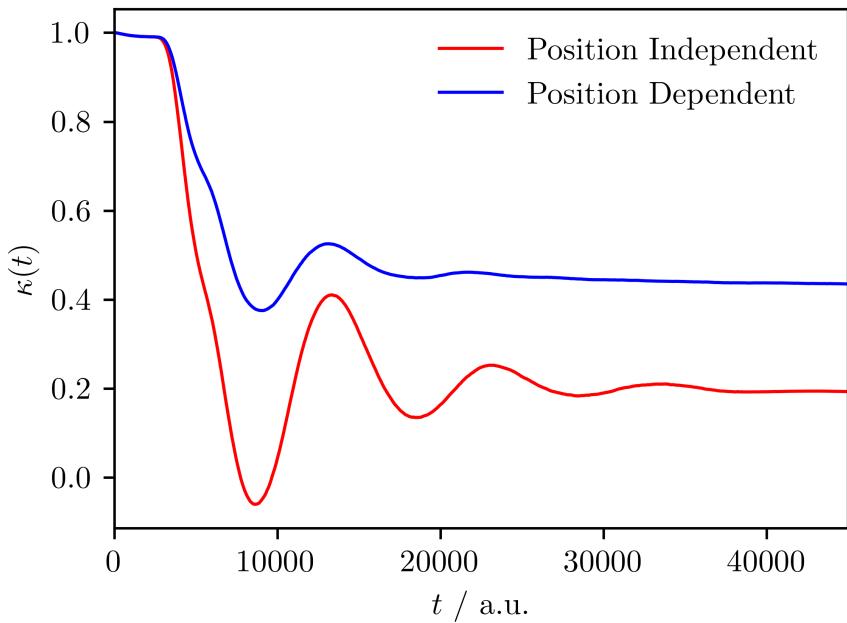
- Model: 1D projection of the minimum energy pathway for hydrogen hopping in palladium
- Position-dependent spectral density used to determine system-bath frequencies and coupling function – from discretization by Walters, Allen and Makri^[12]

$$J(q, \omega) \rightarrow \begin{cases} \{\omega_i\} \\ f_i(q) \end{cases}$$



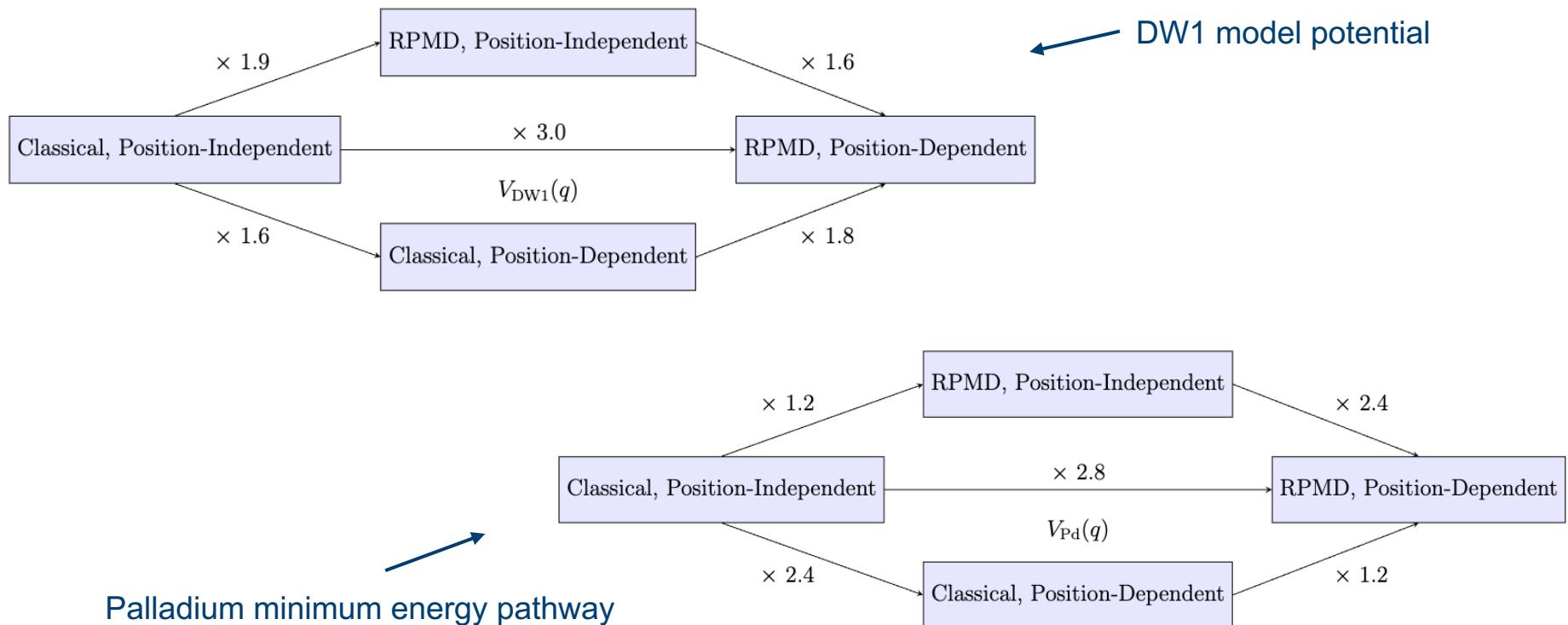
Hydrogen Hopping in Pd – 300K Results

- Interested in the interplay between different factors – position dependence and NQE
- Pd RPMD rates: rate increase from nonlinearity is almost entirely due to the dynamics



Hydrogen Hopping in Pd – 300K Results

- Rate increases – which factors are most important
- Similar trend for potentials that give significantly different rates (~2 orders of magnitude)



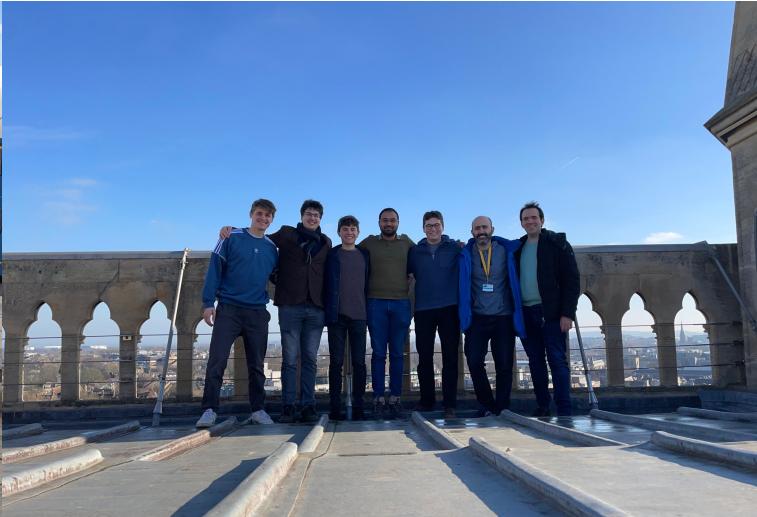
Conclusions and Further Work

- Nonlinear system-bath coupling affects the reaction dynamics in both classical and quantum systems – it favours lower friction at the transition state
- For quantum systems, the free energy additionally contributes to this change
- At room temperature, position-dependent friction is as important as including NQEs in Pd
- Palladium methods are general – may be applied to systems with stronger electronic friction
- Study hydrogen diffusion in palladium in 3D - account for multidimensional NQEs^[14]

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Interpolating from Linear to Nonlinear

