LMG 2 – Dissipative Tunneling Rates through the Incorporation of First-Principles Electronic Friction in Instanton Rate Theory

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Introduction

The modelling of reactions in metallic environments can be very challenging for theory because nuclear quantum effects (NQEs) can play a prominent role and the coupling of the atomic motion with the electrons in the metal gives rise to important non-adiabatic effects (NAEs) that alter atomic dynamics. In this work, we derived the *"ring-polymer instanton with explicit friction"* (**RPI-EF**) method [1, 2] that captures both NQEs and NAEs in such reactions and, due to its high efficiency, can be applied to first-principles calculations of reaction rates in high-dimensional realistic systems.

Ring Polymer Instanton Rate Theory with Explicit Friction

We consider a system coupled to a harmonic bath defined by the spectral density tensor

$$J_{il}(\boldsymbol{q},\omega)=\frac{\pi}{2}\sum_{j=1}^{N_b}\left(\frac{\partial f_{ij}(\boldsymbol{q})}{\partial q_l}\right)^2\frac{1}{\mu_j\omega}(\delta(\omega-\omega_j)+\delta(\omega+\omega_j)),$$

where N_b is the number of bath modes, μ_j and ω_j are the j-th bath oscillator mass and frequency. This allows us to express the time- and position-dependent friction tensor (for $t\geq 0$) as

$$\eta_{il}(\boldsymbol{q},t)=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\frac{J_{il}(\boldsymbol{q},\omega)}{\omega}\cos(\omega t),$$

with the Laplace transform

$$\tilde{\eta}_{il}(\boldsymbol{q},\lambda)=\int_0^{\infty}e^{-\lambda t}\eta_{il}(\boldsymbol{q},t)dt=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\frac{J_{il}(\boldsymbol{q},\omega)}{\omega}\frac{\lambda}{\omega^2+\lambda^2}.$$

Position Dependent Friction

We consider the separable coupling

$$f_{ij}(\boldsymbol{q})=c_j g_i(\boldsymbol{q}),$$

which is equivalent to assuming that $\tilde{\eta}(\boldsymbol{q},\lambda=0)$ is position-dependent and the frequency dependence is identical for all positions. Linear coupling is $g_i(\boldsymbol{q})=q_i$.

After some mathematical manipulation and integration over the bath DOFs, we find the expression

$$U_P^{\text{eff}}=\sum_{k=1}^{P}\sum_{i=1}^{3N}m_i\frac{\omega_P^2}{2}(q_i^{(k)}-q_i^{(k+1)})^2+\sum_{k=1}^{P}V(\boldsymbol{q}^{(k)})+\sum_{l=-P/2+1}^{P/2}\sum_{i=1}^{3N}\frac{\omega_l}{2}\left[\sum_{k=1}^{P}C_{lk}\left(\int_{\boldsymbol{q}^{\text{ref}}}^{\boldsymbol{q}^{(k)}}\tilde{\boldsymbol{\eta}}_i(\boldsymbol{q}',\omega_k)^{1/2}\cdot d\boldsymbol{q}'\right)\right]^2, \quad (1)$$

where $q_i^{(k)}$ is the position of the i-th degree of freedom of the k-th system replica, m_i is the mass, N is the number of atoms, P is the number of replicas, $\omega_P=(\beta_P\hbar)^{-1}$ with $\beta_P=1/(k_BPT)$, $\tilde{\boldsymbol{\eta}}_i$ is the i-th row of the friction tensor and q^{ref} is a free parameter which does not affect the results.

The RPI-EF rate is

$$k_{\text{inst}}^{\text{RPI-EF}}(\beta)=\lim_{P\to\infty}C(\beta_P,\bar{\boldsymbol{q}})e^{-S_P^{\text{eff}}(\bar{q})/\hbar},$$

where $C(\beta_P,\bar{\boldsymbol{q}})$ is an analytical function [3] and $S_P^{\text{eff}}(\bar{\boldsymbol{q}})/\hbar=\beta_P U_P^{\text{eff}}(\bar{\boldsymbol{q}})$ and $\bar{\boldsymbol{q}}$ is the instanton geometry found through a saddle-point optimization of Eq. 1.

Ab initio electronic friction

The adiabatic electronic friction tensor can be obtained from first-principles simulations assuming non-interacting electrons and adopts the following form for $t>0$

$$\eta_{ij}^{\text{el}}(\boldsymbol{q},t)=\hbar\sum_{\nu,\nu'}\langle\psi_\nu|\partial_i\psi_{\nu'}\rangle\langle\psi_{\nu'}|\partial_j\psi_\nu\rangle\,\Omega_{\nu\nu'}\times(f(\epsilon_\nu)-f(\epsilon_{\nu'}))\cos(\Omega_{\nu\nu'}t),$$

where $f(\epsilon)$ is the Fermi-Dirac function, $\Omega_{\nu\nu'}=(\epsilon_{\nu'}-\epsilon_\nu)/\hbar$, ψ_ν and ϵ_ν are the Kohn-Sham orbitals and energies of the ν-th level and $\partial_i=\partial/\partial q_i$. A Laplace transform leads to

$$\tilde{\eta}_{ij}^{\text{el}}(\boldsymbol{q},\lambda)=\hbar\sum_{\nu,\nu'}\langle\psi_\nu|\partial_i\psi_{\nu'}\rangle\langle\psi_{\nu'}|\partial_j\psi_\nu\rangle\,(f(\epsilon_\nu)-f(\epsilon_{\nu'}))\times\Omega_{\nu\nu'}\frac{\lambda}{\lambda^2+\Omega_{\nu\nu'}^2}, \quad (2)$$

which *provides a seamless connection between RPI-EF and electronic friction* and requires no artificial broadening of the spectral density.

Analytical Relations

Extension of Grote-Hynes Theory to Deep Tunneling

For the special case of linear coupling $[f_{ij}(\boldsymbol{q})=c_jq_i]$ and a parabolic barrier, we could prove the following relation

$$T_b/T_c^\circ=\sqrt{\left(\frac{\tilde{\eta}(\omega_l^b)}{2m_i\omega^\ddagger}\right)^2\frac{1}{l^2}+\left(\frac{T_a}{T_c^\circ}\right)^2}-\frac{\tilde{\eta}(\omega_l^b)}{2m_i\omega^\ddagger}\frac{1}{l}, \quad (3)$$

where $l\neq 0$ is the RP normal-mode index, $\omega^\ddagger$ is the imaginary frequency at the barrier top and $T_c^\circ=\frac{\hbar\omega^\ddagger}{2\pi k_B}$ (the crossover temperature).

Calculating an instanton rate (k_{inst}) at T_b given by the relation above allows a full-fledged $k_{\text{inst}}^{\text{RPI-EF}}$ evaluation without further simulations. The equation can be solved by assuming $l=1$ (dominant term) and through a self-consistent procedure ($\omega_l^b=\omega_l(T_b)$).

Renormalization of Crossover Temperature

For the general case and a parabolic barrier, the crossover temperature, below which tunneling can take place, is renormalized in the presence of dissipation by

$$T_c^{\text{sb}}=T_c^\circ\times\left[\sqrt{\left(\frac{\tilde{\eta}(\omega_1)}{2m\omega^\ddagger}\right)^2+1}-\frac{\tilde{\eta}(\omega_1)}{2m\omega^\ddagger}\right],$$

which means that tunneling is suppressed. This can also be derived from Eq. 3 for $l=1$ and $T_a=T_c^\circ$.

Results: Linear Coupling

Model double-well (DW) potential given by

$$V_{\text{DW}}(q)=-\frac{1}{2}m\omega^{\ddagger 2}(q-q_0)^2+\frac{m^2\omega^{\ddagger 4}}{16V_0}q^4,$$

with $m=m_p$ and $\omega^\ddagger=500$ cm^{-1}. The system-bath coupling is

$$f(q)=q[1+\epsilon_1\exp(-\Delta q^2/2)+\epsilon_2\tanh(\Delta q)], \quad (4)$$

where $\Delta q=(q-q^\ddagger)/\delta$. Linear coupling obtained with $\epsilon_1=\epsilon_2=0$.

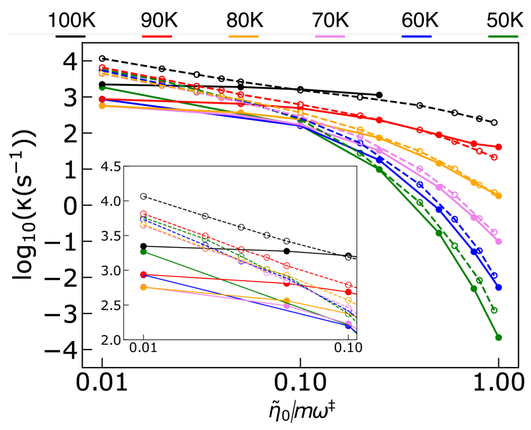

Figure 1: Benchmarks. Reaction rates on V_{DW} ($V_0=258$ meV, $\omega_c=500$ cm^{-1} and $q_0=0$) computed with RPI-EF (solid lines with filled circles) and multi-layer multi-configuration time-dependent Hartree method (dashed lines with empty circles).

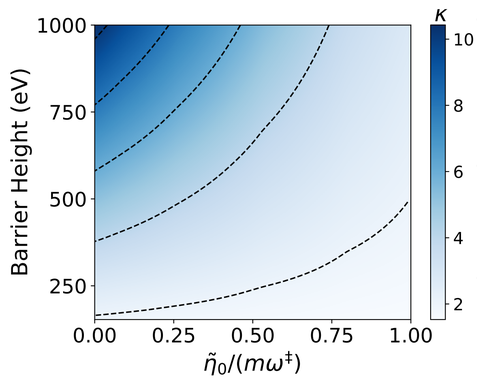

Figure 2: Tunneling enhancement factors $\log_{10}[\kappa(\beta,\tilde{\eta}_0)]$ as a function of energy barrier height and friction strength. DW potential with $q_0=0.08$ Å (asymmetric reaction profile) at $T=0.7T_c^\circ$. Contour lines represent isosurfaces spaced by 2 logarithmic units.

- Good agreement with benchmarks for medium and high friction strengths
- "Intrinsic" dissipation in RPI-EF at low friction strengths
- Tunneling enhancement factor increases with barrier height and decreases with increasing friction strength
- Most H diffusion in metals map to values on bottom-left of Fig. 2.

References

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Results: Position Dependence

Two-dimensional double double-well (DDW) potential

$$V_{\text{DDW}}(q_1,q_2)=V_{\text{DW}}(q_1)+V_{\text{DW}}(q_2)+Cq_1q_2,$$

where C is a constant to be specified. The coupling function is given by $f(q_1,q_2)=(f(q_1),f(q_2))$ where $f(q_i)$ is given by Eq. 4.

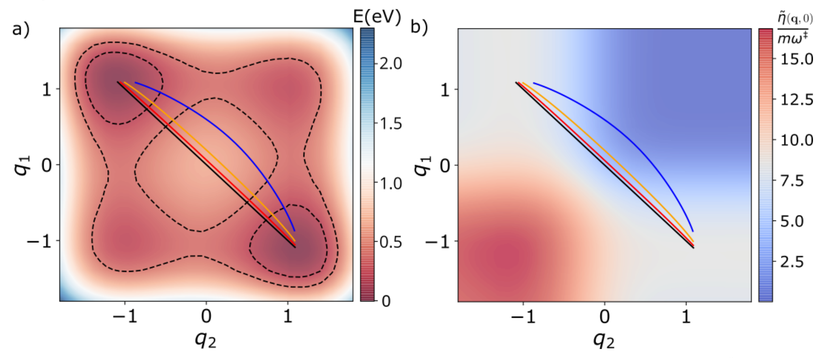

Figure 3: Instanton pathways on the DDW model ($V_0=258$ meV, $q_0=0$ Å, $C=97.1$ meV/Å^2, $\epsilon_1=0$, $\epsilon_2=-0.8$, and $\Delta=1.0$). $\tilde{\eta}_0/m\omega^\ddagger=0$, 0.10, 0.25, and 0.50 shown as full black, red, orange, and blue lines. The pathways are shown on a) the underlying potential energy surface and b) the (position-dependent) value of the friction tensor. The map is computed as the sum of the diagonal elements of $\tilde{\eta}$ for $\tilde{\eta}_0/m\omega^\ddagger=0.50$.

- Anisotropy of the friction modifies the instanton pathway (bends towards lower friction)
- Dissipative tunneling: compromise between path with shortest length, lowest potential energy, and lowest friction.

Ab initio H hopping in Pd bulk

Bulk Pd with 2 x 2 x 2 cubic supercells, containing one H or D atom. Energies and forces from density-functional theory (DFT) from the FHI-aims [4] code and PBE functional. Electronic friction tensor was computed through Eq. 2 and non-adiabatic couplings were obtained by finite-differences [5].

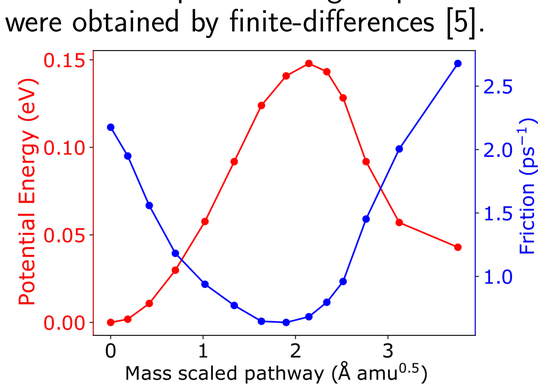

Figure 4: Minimum energy pathway (MEP) and friction along the reaction coordinate for the H hopping reaction in Pd (PBE functional). The energy is set to zero at the reactant geometry.

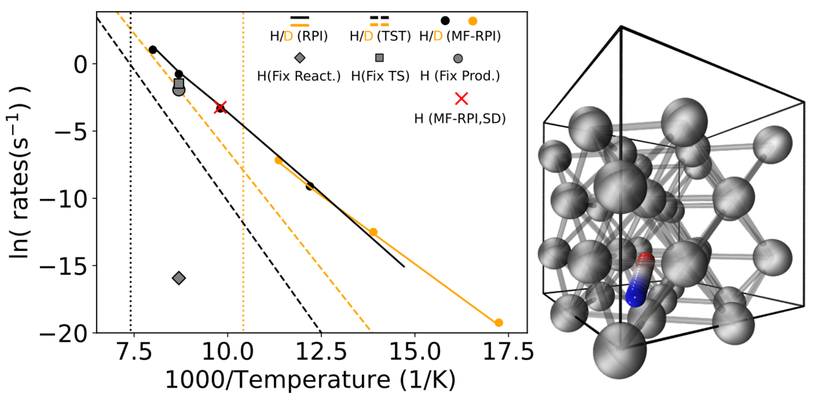

Figure 5: Reaction rates for octahedral→tetrahedral-site hopping reaction of H (black) and D (orange) in Pd, calculated by transition state theory (dashed lines), and RPI rate theory (solid lines). RPI-EF rates with friction fixed at a value of 4 ps^{-1} are black and orange circles (H and D, respectively). RPI-EF rate with position-dependent friction is the red cross. RPI rate calculations with the Pd atoms fixed at their reactant, transition and product states are presented by diamond, square and circle gray symbols, respectively. T_c° for H and D are marked by vertical black and orange dotted lines. The interstitial hopping of H in Pd is depicted on the right.

Conclusions

- Efficient methodology that allows calculation of fully atomistic *ab initio* dissipative tunneling rates
- Suppression of tunneling for high $\tilde{\eta}$ and high energy barriers
- Tunneling path deformed towards region of low friction
- Multidimensional vibrational coupling and NQEs have a larger impact than NAEs on the tunneling rates of H diffusion in metals
- NAEs more relevant for tunneling of impurities or adsorbates with electronic levels close to the metal Fermi energy

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