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Nonadiabatic rate theory

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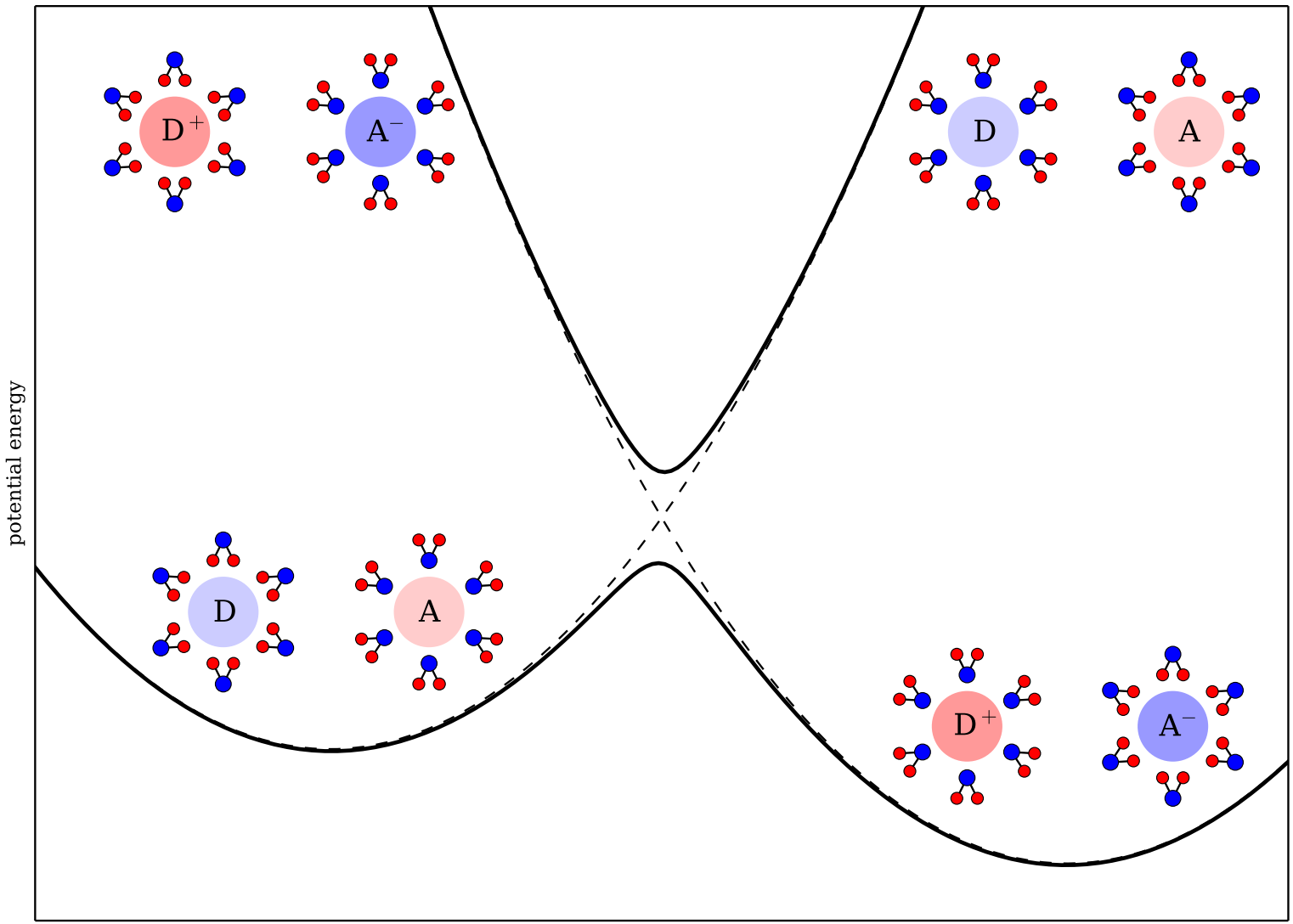
Recap

- Path integrals describe quantum nuclear statistics (and some dynamical aspects) within Born-Oppenheimer approximation (i.e. a single potential-energy surface)

- Instanton theory is derived to give rate for reaction through a potential barrier

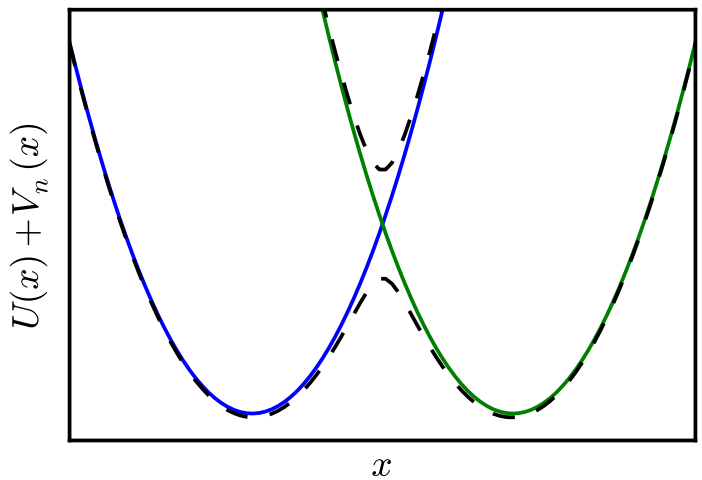
- Steepest-descent approximation can be treat integration over real time in a simple way, requiring only information at $t = 0$ which can be computed efficiently

Electron-transfer in solution



Diabatic representation

$$\hat{H} = \frac{\hat{p}^2}{2m} + \begin{pmatrix} V_0(\hat{x}) & \Delta(\hat{x}) \\ \Delta(\hat{x}) & V_1(\hat{x}) \end{pmatrix}$$



- diabatic states shown in blue/green
- coupling, Δ, is found in potential terms
- weak coupling means you are likely to stay on the same diabatic state (i.e. change adiabatic state)

Adiabatic representation

$$\hat{H} = \frac{\hat{p}^2}{2m} + W(\hat{x}) - \frac{\hbar^2}{2m}(2\hat{\mathsf{F}} \cdot \nabla + \hat{\mathsf{G}})$$

$$W_{nm} = W_n \delta_{nm} \qquad \text{diagonal matrix of eigenvalues of } \mathsf{V}$$

$$\hat{F}_{nm} = \langle \phi_n | \nabla \phi_m \rangle$$

$$\hat{G}_{nm} = \langle \phi_n | \nabla^2 \phi_m \rangle$$

- avoided crossing of adiabatic states (black dashed in previous figure)
- coupling in kinetic terms
- weak coupling means you are likely to stay on the same adiabatic state (i.e. change diabatic state)
- We will use diabatic representation in the following as it is simpler

Mean-field path-integral sampling

$$
\begin{aligned}
Z &= \mathrm{Tr}[\mathrm{e}^{-\beta \hat{H}}] \\
&\simeq \mathrm{Tr}\left[\prod_{i=1}^{N} \mathrm{e}^{-\beta_N \hat{\mathsf{V}}/2} \mathrm{e}^{-\beta_N \hat{p}^2/2m} \mathrm{e}^{-\beta_N \hat{\mathsf{V}}/2}\right]
\end{aligned}
$$

Only difference from Born-Oppenheimer case is that $\mathsf{V}(x)$ is a matrix and the trace is taken over position and electronic states.

$$
Z \simeq \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{e}^{-\beta_N U_N(\mathbf{x})} \mathrm{d}\mathbf{x}
$$

$$
U_N(\mathbf{x}) = \sum_{i=1}^{N} \frac{m}{2\beta_N^2\hbar^2} |x_i - x_{i-1}|^2 - \frac{1}{\beta_N} \ln \mathrm{tr}\left[\prod_{i=1}^{N} \mathrm{e}^{-\beta_N \mathsf{V}(x_i)}\right].
$$

Mean-field path-integral sampling

Closer look at product of matrix exponentials:

$$\mathrm{tr}\left[\prod_{i=1}^{N} \mathrm{e}^{-\beta_N \mathsf{V}(x_i)}\right] = \sum_{abcd\ldots z} [\mathrm{e}^{-\beta_N \mathsf{V}(x_1)}]_{ab} [\mathrm{e}^{-\beta_N \mathsf{V}(x_2)}]_{cd} \cdots [\mathrm{e}^{-\beta_N \mathsf{V}(x_N)}]_{za}$$

The matrix exponential is easily evaluated on the computer (e.g. using Padé approximation or eigenvalue decomposition). The result is approximately equal to (derived from splitting operator into diagonal and non-diagonal elements):

$$\mathrm{e}^{-\beta_N \mathsf{V}} \approx \begin{pmatrix} \mathrm{e}^{-\beta_N V_0} & -\beta_N \Delta \mathrm{e}^{-\beta_N (V_0+V_1)/2} \\ -\beta_N \Delta \mathrm{e}^{-\beta_N (V_0+V_1)/2} & \mathrm{e}^{-\beta_N V_1} \end{pmatrix}$$

- For each term in sum, some beads feel blue potential, others feel green
- Each time you change state, you introduce a factor of Δ

Why can't we use mean-field ring-polymer molecular dynamics?

$$H_N(\mathbf{p},\mathbf{x}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{m}{2\beta_N^2\hbar^2}|x_i - x_{i-1}|^2 - \frac{1}{\beta_N} \ln \mathrm{tr} \left[\prod_{i=1}^{N} \mathrm{e}^{-\beta_N \mathsf{V}(x_i)} \right].$$

Consider:

- Zero coupling, $\Delta = 0$
- Initial position on left (electronic state blue)
- System should remain for all time on blue state as it is not coupled to green
- However, the mean-field RPMD trajectory can pass over to the right if it has enough energy to overcome the barrier changing directly from all blue to all green without penalty

Exact nonadiabatic rate

Probability of transmission:

$$P(E) = 2\pi^2\hbar^2 \,\mathrm{Tr}[\hat{F}\delta(\hat{H}-E)\hat{F}\delta(\hat{H}-E)]$$

Flux:

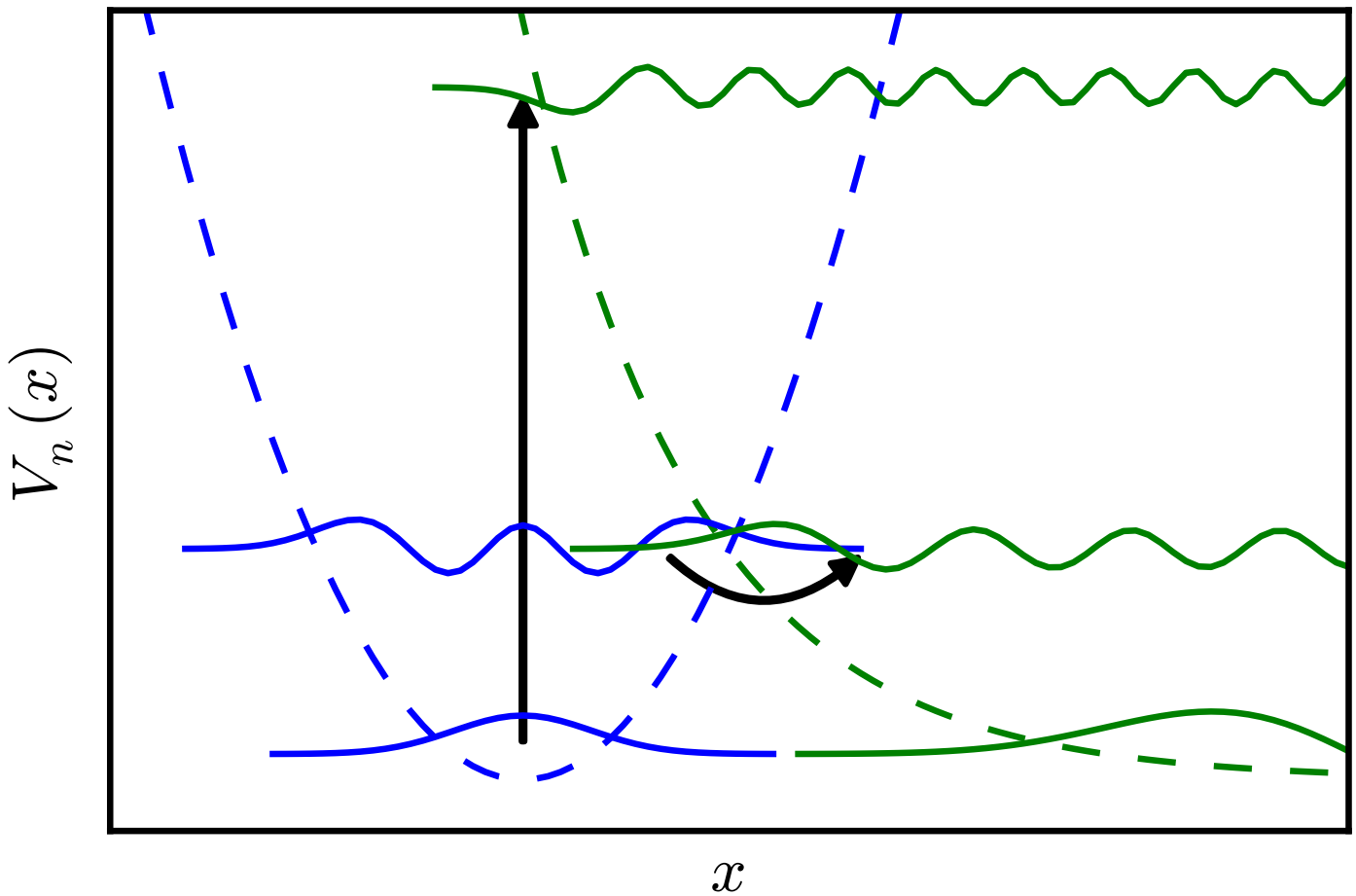
$$\hat{F} = \frac{\mathrm{i}}{\hbar}\Delta\big(\,|0\rangle\langle 1| - |1\rangle\langle 0|\,\big)$$

Thermal rate:

$$kZ_0 = \frac{1}{2\pi\hbar}\int P(E)\,\mathrm{e}^{-\beta E}\,\mathrm{d}E$$

Fermi's golden rule

$$P(E) = 4\pi^2 \Delta^2 \left| \langle \psi_0(E) | \psi_1(E) \rangle \right|^2$$



Alternative formulation of the exact nonadiabatic rate

$$\delta(\hat{H}-E)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\mathrm{e}^{-\mathrm{i}(\hat{H}-E)t/\hbar}\mathrm{d}t$$

$$\begin{aligned}
kZ_0 &= \frac{2\pi^2\hbar^2}{2\pi\hbar}\int \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}\hat{F}\delta(\hat{H}-E)\hat{F}\delta(\hat{H}-E)]\,\mathrm{d}E \\
&= \frac{2\pi^2\hbar^2}{(2\pi\hbar)^3}\iiint \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}\hat{F}\mathrm{e}^{-\mathrm{i}(\hat{H}-E)z/\hbar}\hat{F}\mathrm{e}^{-\mathrm{i}(\hat{H}-E)t/\hbar}]\,\mathrm{d}E\mathrm{d}z\mathrm{d}t \\
&= \frac{2\pi^2\hbar^2}{(2\pi\hbar)^3}\iiint \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}\hat{F}\mathrm{e}^{-\mathrm{i}\hat{H}z/\hbar}\hat{F}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}]\mathrm{e}^{-\mathrm{i}E(-z-t)/\hbar}\,\mathrm{d}E\mathrm{d}z\mathrm{d}t \\
&= \frac{2\pi^2\hbar^2}{(2\pi\hbar)^2}\iint \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}\hat{F}\mathrm{e}^{-\mathrm{i}\hat{H}z/\hbar}\hat{F}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}]\delta(z+t)\,\mathrm{d}z\mathrm{d}t \\
&= \frac{1}{2}\int \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}\hat{F}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{F}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}]\,\mathrm{d}t
\end{aligned}$$

Alternative formulation of the exact nonadiabatic rate

As in the Born-Oppenheimer case, the exact rate can be written as an integral over the flux-flux correlation function:

$$kZ_0 = \frac{1}{2}\int_{-\infty}^{\infty} C_{FF}(t)\,\mathrm{d}t,$$

where the flux-flux correlation function is

$$C_{FF}(t) = \mathrm{Tr}[\mathrm{e}^{-\tau\hat{H}}\hat{F}\mathrm{e}^{-(\beta-\tau)\hat{H}}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{F}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}]$$

- Rate is exact for any value of τ as this is equivalent to choosing different contour integrations in the t complex plane

Fermi's golden rule

Take limit $\Delta \ll 1$.

$$
\begin{aligned}
C_{FF}(t) = & \frac{\Delta^2}{\hbar^2} \operatorname{Tr}[\mathrm{e}^{-\tau \hat{H}} |0\rangle\langle 1| \mathrm{e}^{-(\beta-\tau)\hat{H}} \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} |1\rangle\langle 0| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}] \\
& + \frac{\Delta^2}{\hbar^2} \operatorname{Tr}[\mathrm{e}^{-\tau \hat{H}} |1\rangle\langle 0| \mathrm{e}^{-(\beta-\tau)\hat{H}} \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} |0\rangle\langle 1| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}] \\
& = \frac{\Delta^2}{\hbar^2} \operatorname{Tr}[\mathrm{e}^{-\tau \hat{H}_0} \mathrm{e}^{-(\beta-\tau)\hat{H}_1} \mathrm{e}^{\mathrm{i}\hat{H}_1 t/\hbar} \mathrm{e}^{-\mathrm{i}\hat{H}_0 t/\hbar}] \\
& + \frac{\Delta^2}{\hbar^2} \operatorname{Tr}[\mathrm{e}^{-\tau \hat{H}_1} \mathrm{e}^{-(\beta-\tau)\hat{H}_0} \mathrm{e}^{\mathrm{i}\hat{H}_0 t/\hbar} \mathrm{e}^{-\mathrm{i}\hat{H}_1 t/\hbar}]
\end{aligned}
$$

Only after integrating over t do the two terms give equal results, so you only need to consider one of them (multiplied by 2) to get the rate

Classical golden-rule rate

$$kZ_0 = \frac{\Delta^2}{\hbar^2} \int \mathrm{Tr}[\mathrm{e}^{-\tau \hat{H}_0} \mathrm{e}^{-(\beta-\tau)\hat{H}_1} \mathrm{e}^{\mathrm{i}\hat{H}_1 t/\hbar} \mathrm{e}^{-\mathrm{i}\hat{H}_0 t/\hbar}] \mathrm{d}t \, \mathrm{d}t$$

In the classical limit, replace operators by classical numbers:

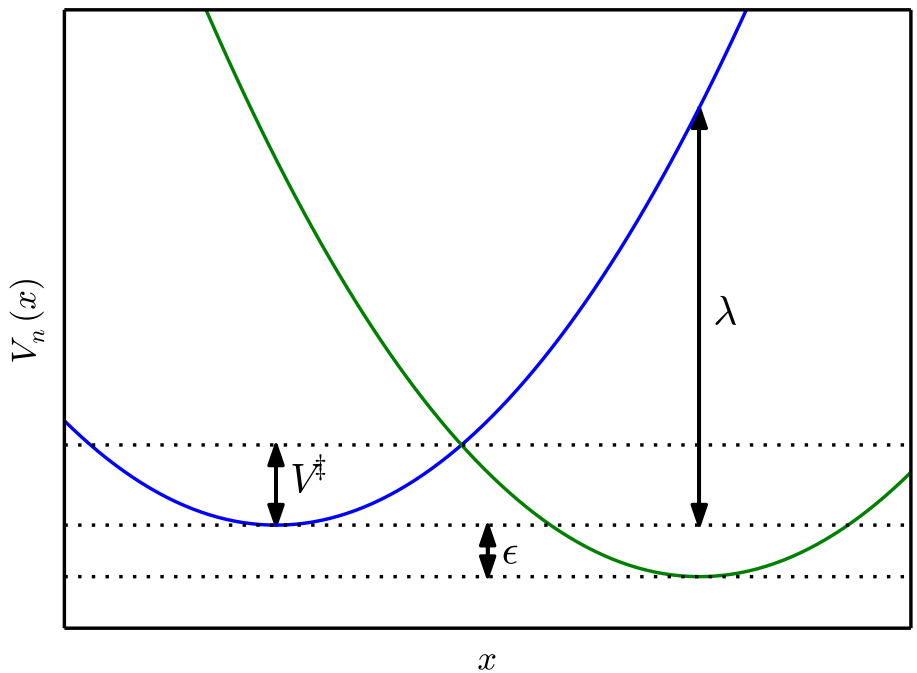
$$\begin{aligned} kZ_0 &= \int \frac{\Delta^2}{\hbar^2} \mathrm{Tr}[\mathrm{e}^{-\tau H_0 - (\beta-\tau)H_1} \mathrm{e}^{\mathrm{i}(H_1 - H_0)t/\hbar}] \, \mathrm{d}t \\ &= 2\pi\hbar \frac{\Delta^2}{\hbar^2} \mathrm{Tr}[\mathrm{e}^{-\tau H_0 - (\beta-\tau)H_1} \delta(H_1 - H_0)] \\ &= \frac{\Delta^2}{\hbar^2} \iint \mathrm{e}^{-\tau H_0 - (\beta-\tau)H_1} \delta(V_1 - V_0) \mathrm{d}x \mathrm{d}p \end{aligned}$$

- classical rate depends exponentially on barrier height
- the top of the barrier is defined at the lowest-energy configuration where $V_0 = V_1$.

Marcus theory

- for harmonic system
- $V_0(x) = \frac{1}{2}m\Omega^2(x+\xi)^2$ and $V_1(x) = \frac{1}{2}m\Omega^2(x-\xi)^2 - \epsilon$
- with reorganization energy $\lambda = 2m\Omega^2\xi^2$

$$k_{\text{Marcus}} = \frac{\Delta^2}{\hbar}\sqrt{\frac{\pi\beta}{\lambda}}\,\mathrm{e}^{-\beta(\lambda-\epsilon)^2/4\lambda}$$



Golden-rule instanton rate theory

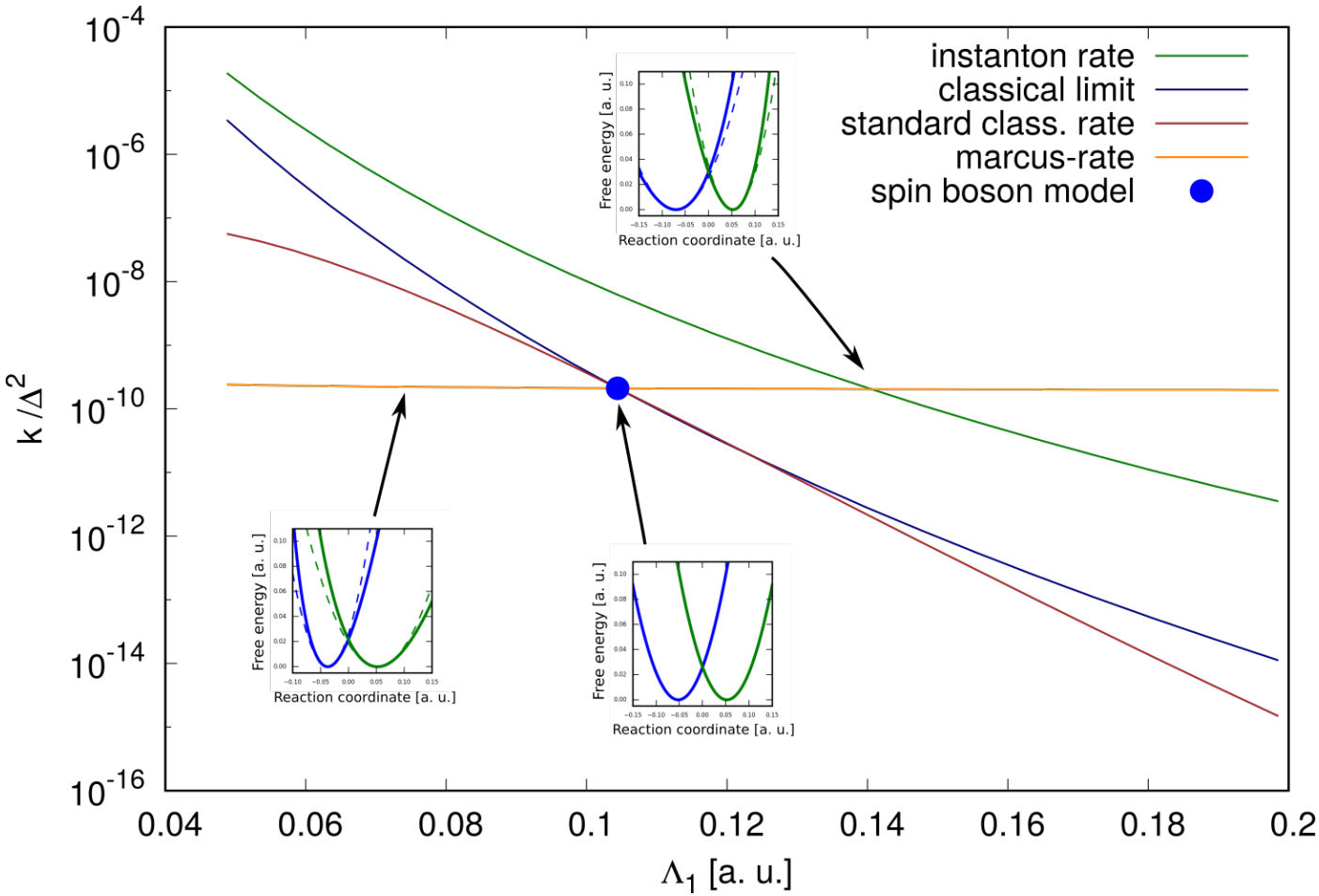
Take limit $\Delta \ll 1$. Define $\tau_0 \equiv \tau$ and $\tau_1 \equiv \beta\hbar - \tau$,

$$
\begin{aligned}
kZ_0 &= \frac{\Delta^2}{\hbar^2} \int \mathrm{Tr}[\mathrm{e}^{-(\tau_0 + \mathrm{i}t)\hat{H}_0/\hbar} \mathrm{e}^{-(\tau_1 - \mathrm{i}t)\hat{H}_1/\hbar}] \mathrm{d}t \\
&= \frac{\Delta^2}{\hbar^2} \iiint K_0(x', x'', \tau_0 + \mathrm{i}t) K_1(x'', x', \tau_1 - \mathrm{i}t) \mathrm{d}x' \mathrm{d}x'' \mathrm{d}t \\
&\sim \frac{\Delta^2}{\hbar^2} \sqrt{\frac{C_0}{2\pi\hbar}} \sqrt{\frac{C_1}{2\pi\hbar}} \sqrt{\frac{2\pi\hbar}{-\Sigma}} \, \mathrm{e}^{-(S_0 + S_1)/\hbar}
\end{aligned}
$$

where $S = S_0 + S_1$, τ is chosen such that $\frac{\partial S}{\partial \tau} = 0$, and

$$
\Sigma = \begin{vmatrix}
\frac{\partial^2 S}{\partial x' \partial x'} & \frac{\partial^2 S}{\partial x' \partial x''} & \frac{\partial^2 S}{\partial x' \partial \tau} \\
\frac{\partial^2 S}{\partial x'' \partial x'} & \frac{\partial^2 S}{\partial x'' \partial x''} & \frac{\partial^2 S}{\partial x'' \partial \tau} \\
\frac{\partial^2 S}{\partial \tau \partial x'} & \frac{\partial^2 S}{\partial \tau \partial x''} & \frac{\partial^2 S}{\partial \tau^2}
\end{vmatrix} .
$$

Asymmetric system-bath model



- Mattiat & J.O.R. "Effects of tunnelling and asymmetry for system-bath models of electron transfer." *J. Chem. Phys.* **148**, 102311 (2018); arXiv:1708.06702 [physics.chem-ph].

Wolynes theory

Take limit $\Delta \ll 1$. Define $\tau_0 \equiv \tau$ and $\tau_1 \equiv \beta\hbar - \tau$,

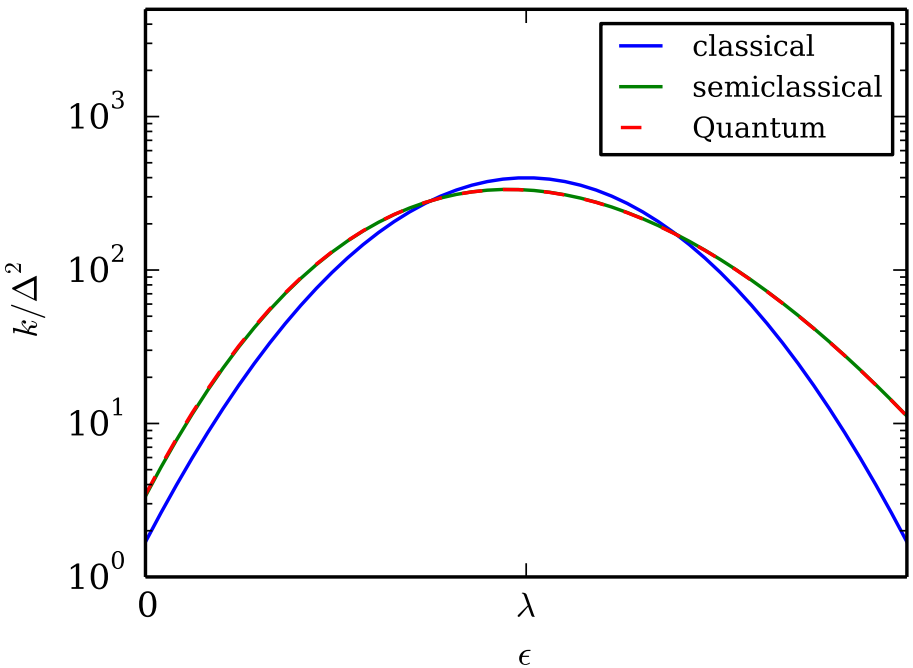
$$\begin{aligned} kZ_0 &= \frac{\Delta^2}{\hbar^2} \int \mathrm{Tr}[\mathrm{e}^{-(\tau_0 + \mathrm{i}t)\hat{H}_0/\hbar} \mathrm{e}^{-(\tau_1 - \mathrm{i}t)\hat{H}_1/\hbar}] \mathrm{d}t \\ &= \frac{\Delta^2}{\hbar^2} \int \mathrm{e}^{-\phi(t)/\hbar} \mathrm{d}t \\ &\approx \frac{\Delta^2}{\hbar^2} \sqrt{\frac{2\pi\hbar}{-\phi''(0)}} \mathrm{e}^{-\phi(0)/\hbar} \end{aligned}$$

where

$$\mathrm{e}^{-\phi(0)/\hbar} = \Lambda^N \int \mathrm{e}^{-S_0(x_0,\ldots,x_{N_0})/\hbar - S_1(x_{N_0},\ldots,x_N)/\hbar} \mathrm{d}\mathbf{x}$$

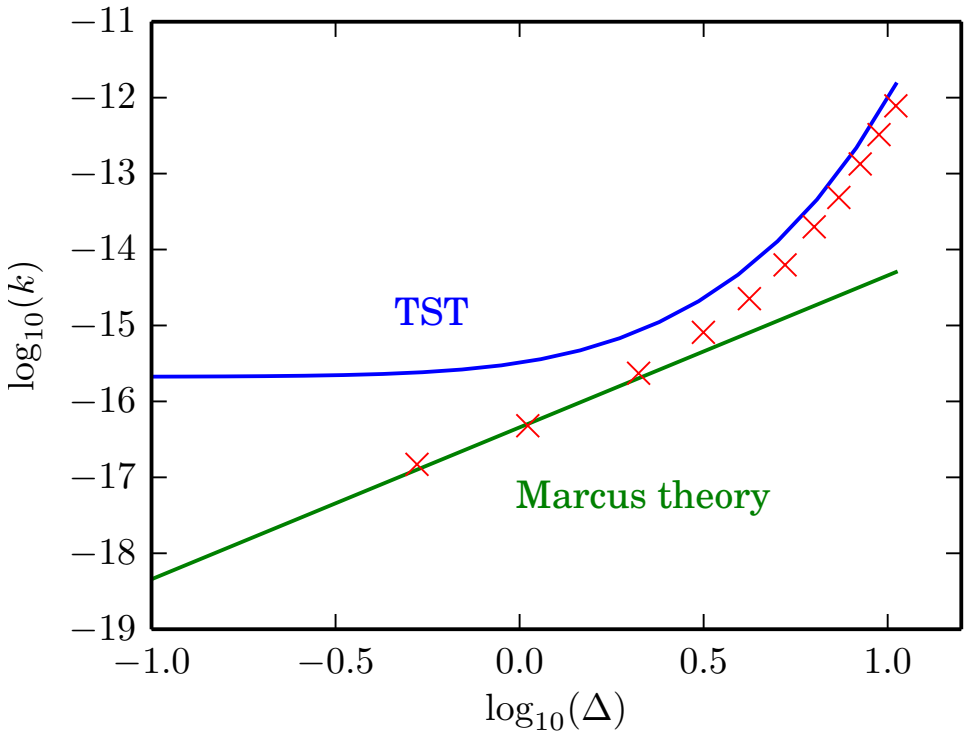
- ϕ defined with optimal τ such that $\phi'(0) = 0$
- Steepest-descent integration over t but not $\mathbf{x}$
- Not a true asymptotic approximation (because ϕ depends on $\hbar$) so not exact in $\hbar \to 0$ limit, except for harmonic model.

Marcus turnover curve



- Increasing the bias lowers the barrier height and increases the rate
- Once the bias is larger than the reorganization energy, the barrier height goes back up and the rate decreases
- The difference between classical and quantum is mostly due to tunnelling effects, which are well described by instanton theory

Results



- Effect of changing coupling strength in system with a potential barrier (see also talk by Joe Lawrence)
- small Δ is well described by Fermi's golden rule
- large Δ is well described by Born-Oppenheimer

Summary of most important concepts

- Diabatic representation simpler than adiabatic (when it is available)
- Mean-field path-integral used for sampling but not dynamics
- Fermi's golden-rule is valid in small Δ limit;
  Born-Oppenheimer TST is valid in large Δ limit
- Golden-rule instanton theory derived from first principles
- Wolynes theory (like the related "quantum instanton" theory) is less rigorous and will not tend to correct classical limit

Reading List

- Wolynes. "Imaginary time path integral Monte Carlo route to rate coefficients for nonadiabatic barrier crossing." *J. Chem. Phys.* **87**, 6559 (1987).
- J.O.R., Bauer & Thoss. "Semiclassical Green's functions and an instanton formulation of electron-transfer rates in the nonadiabatic limit." *J. Chem. Phys.* **143**, 134115 (2015); arXiv:1508.04919 [physics.chem-ph].
- J.O.R. "Ring-polymer instanton theory of electron transfer in the nonadiabatic limit." *J. Chem. Phys.* **143**, 134116 (2015); arXiv:1508.05195 [physics.chem-ph].