Calculation of quantum barrier crossing rates in dissipative environments:

A non-Markovian density matrix approach

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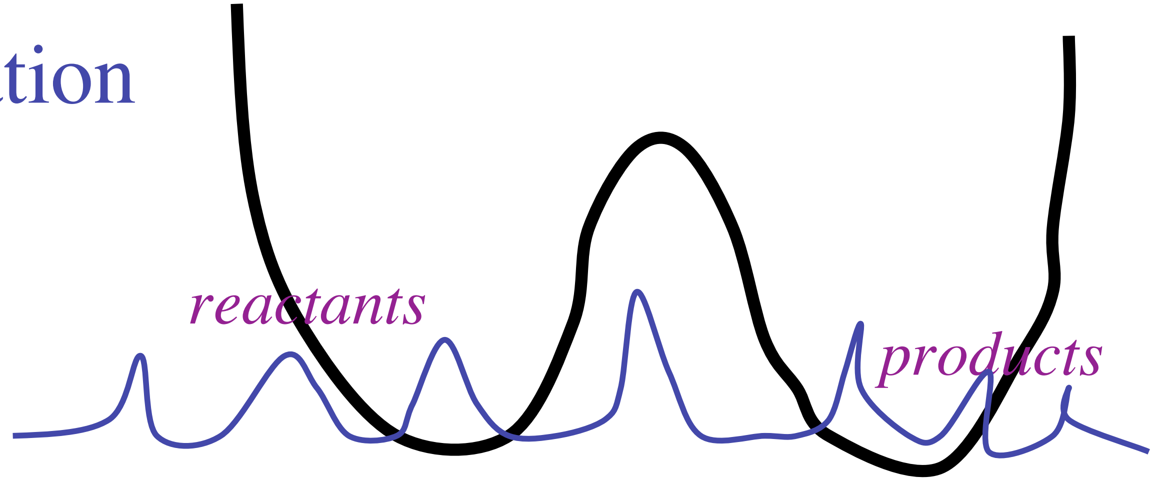
Motivation



•The calculation of quantum reaction rates in solution phase is a central challenge of theoretical chemistry

•Path integral methods provide an exact procedure, but are computationally costly, and impractical for large *N*-level systems

•Mixed classical-quantum methods are accurate at high *T* but deteriorate at low *T*

•QME methods are very intuitive and treat the system quantum mechanically, but are derived under weak friction assumptions

Outline

1. *Review of NM-QME*
2. *Calculation of reaction rates using the NM-QME*
3. *QME in the collective mode representation (*QME-CM*)*
4. *Results*

1. Review of the NM-QME ---- Preliminaries

$$H = \frac{\boldsymbol{p}^2}{2M} + W(\boldsymbol{x}) + \sum_{j=1}^{N} [\frac{p^2}{2m_j} + \frac{1}{2} m_j \omega_j (x_j - \frac{\varepsilon c_j}{m_j \omega_j} f(\boldsymbol{x}))^2]$$

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{c_j^{\ 2}}{m_j \omega_j} [\delta(\omega - \omega_j) + \delta(\omega + \omega_j)]$$

$$\gamma(t) = \frac{2}{M} \int_0^{\infty} \frac{d\omega}{\pi} \frac{J(\omega)}{\omega} \cos(\omega t)$$

$$c(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} J(\omega) \cos(\omega t) \coth(\frac{\beta\omega}{2}) \ -i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} J(\omega) \sin(\omega t)$$

$$= a(t) - ib(t)$$

NM-QME: *Equations of Motion*

$$\rho_s = \mathrm{Tr}_b[\rho]$$

$$\dot{\rho}_s(t) = -i\mathcal{L}_s^{eff}\rho_s(t) + \int_{-\infty}^{t} dt' K(t-t')\rho_s(t')$$

$$K(t-t') = \mathcal{L}_- e^{-i\mathcal{L}t}\left[a(t-t')\mathcal{L}_- - ib(t-t')\mathcal{L}_+\right]$$

$$\mathcal{L}_s = \frac{1}{\hbar}[H_s,\cdot] \qquad \mathcal{L}_- = \frac{1}{\hbar}[x,\cdot] \qquad \mathcal{L}_+ = \frac{1}{\hbar}\{x,\cdot\}$$

$$\mathcal{L}_s^{eff} = \frac{1}{\hbar}\left(H_s + \frac{\mu}{2}x^2\right) \qquad \mu = \int_0^{\infty}\frac{J(\omega)}{\omega}\,d\omega$$

$$a(t) = \sum_{j=1}^{n_r} \alpha_j^r e^{-\gamma_j^r t} \qquad b(t) = \sum_{j=1}^{n_i} \alpha_j^i e^{-\gamma_j^i t}$$

By expansion of *c(t)* in terms of complex exponents
may be recast into a set of coupled simultaneous equations:

$$\dot{\rho}_s(t) = -i\, L_s^{\text{eff}} \rho_s(t) + \varepsilon L_- \left(\sum_{j=1}^{n_r} \alpha_j^r \rho_j^r(t) - i \sum_{j=1}^{n_i} \alpha_j^i \rho_j^i(t)\right)$$

$$\dot{\rho}_j^r(t) = \varepsilon\, L_- \rho_s(t) - i(L_s - i\gamma_j^r)\rho_j^r(t), \quad j = 1,\ldots,n_r$$

$$\dot{\rho}_j^i(t) = \varepsilon\, L_+ \rho_s(t) - i(L_s + i\gamma_j^i)\rho_j^i(t), \quad j = 1,\ldots,n_i$$

auxiliary matrices

- Nakajima-Zwanzig procedure in reverse!
- The new coupled equation of motion can be viewed as those of a surrogate Hamiltonian
- Physical interpretation in terms of 2nd-order system-bath interaction
- Correlated initial conditions = nonzero initial auxiliaries!

2. *Calculation of Reaction Rates Using NM-QME*

$$k(T) = \frac{1}{Q_0(T)} \int_0^\infty dt C_{ff}(t) \qquad Q_0 = Tr\left[e^{-\beta \hat{H}_s} \hat{h}\right]$$

$$C_{ff}(t) = Tr_s\left[\hat{F}_s(\beta/2)\hat{F}_s(t,\beta/2)\right]$$

$$\hat{F}_s = \frac{i}{\hbar}[\hat{H}_s, \hat{h}]$$

$$\hat{F}_s(\beta/2) = e^{-\beta \hat{H}_s/4} \hat{F}_s e^{\beta \hat{H}_s/4}$$

$$\hat{F}_s(t,\beta/2) = Tr_b[e^{i\hat{H}t}\left(\hat{F}_s(\beta/2) \otimes \rho_b^{eq}\right) e^{-i\hat{H}t}]$$

- Flux operator is propagated as if *F(β/2)* were an initial density matrix
- Propagation is backwards in time (Heisenberg picture)
- Separable initial conditions

3. QME in the Collective Mode Representation

Original representation:

$$H = \frac{1}{2}p_q^2 + w(q) + \frac{1}{2}\sum_{j=1}^{N}\left[p_j^2 + (\omega_j x_j - \frac{c_j}{\omega_j}q)^2\right]$$

$$w(q) = \underbrace{w(q^\ddagger) - \frac{1}{2}w^{\ddagger 2}(q - q^\ddagger)^2}_{harmonic} \quad + \quad \underbrace{w_1(q)}_{anharmonic}$$

$$H = H_0 + H_1$$

$$H_0 = \frac{1}{2}\mathbf{p}^2 + \frac{1}{2}\mathbf{qKq}$$

2nd representation:

$$\mathbf{UKU^{-1}} = \mathbf{L}^2$$

$-\lambda^{\ddagger 2}$	ρ	1 unstable coordinate
$\{\lambda_j{}^2\}$	$\{y_j\}$	N stable coordinates

$$H_0 = \frac{1}{2}\left(p_\rho^2 - {\lambda^\ddagger}^2 \rho^2 + \sum_{j=1}^{N} p_{y_j}^2 + \sum_{j=1}^{N} \lambda_j^2 y_j^2\right)$$

3rd representation:

Old system coordinate defines collective mode σ:

$$q = u_{00}\rho + \sum_{j=1}^{N} u_{j0} y_j = u_{00}\rho + u_1 \sigma$$

$$H = \frac{1}{2}\left(p_\rho^2 - {\lambda^\ddagger}^2 \rho^2 + p_\sigma^2 + \omega_\sigma^2 \sigma^2\right) + w_1[q(\rho,\sigma)] + \frac{1}{2}\sum_{j=1}^{N-1}\left[p_{r_j}^2 + \left(\omega_j r_j - \frac{h_j}{\omega_j}\sigma\right)\right]^2$$

$$u_1^2 = \sum_{j=1}^{N} u_{j0}^2 = 1 - u_{00}^2 \qquad \omega_\sigma^{-2} = \frac{1}{u_1^2}\sum_{j=1}^{N}\frac{u_{j0}^2}{\lambda_j^2}$$

Comments:

- 1-d system (q) becomes 2-d system (ρ, σ)
- The parameters of the new bath modes are not needed — only the new spectral density or friction, $\gamma_\sigma(t)$
- Can't get $\gamma_\sigma(t)$ but can get

$$\hat{\gamma}_\sigma(s) = F(\mathbf{U}, \mathbf{L}, s) = G(\hat{\gamma}(s), \omega^\ddagger, s) \qquad \text{(continuum limit)}$$

More Comments:

- $\lambda^\ddagger$ is the solution of ${\lambda^\ddagger}^2 + \lambda^\ddagger \hat{\gamma}(\lambda^\ddagger) = {\omega^\ddagger}^2$ (Grote-Hynes frequency) softening of the barrier frequency
- Coupling to the bath is now via the σ coordinate only!
- Example: Drude spectral density

$$J(\omega) = \frac{\epsilon\omega}{1 + (\omega/\omega_c)^2} \longrightarrow \tilde{J}(\omega) = \frac{\tilde{\epsilon}\omega}{1 + (\omega/\tilde{\omega}_c)^2}$$

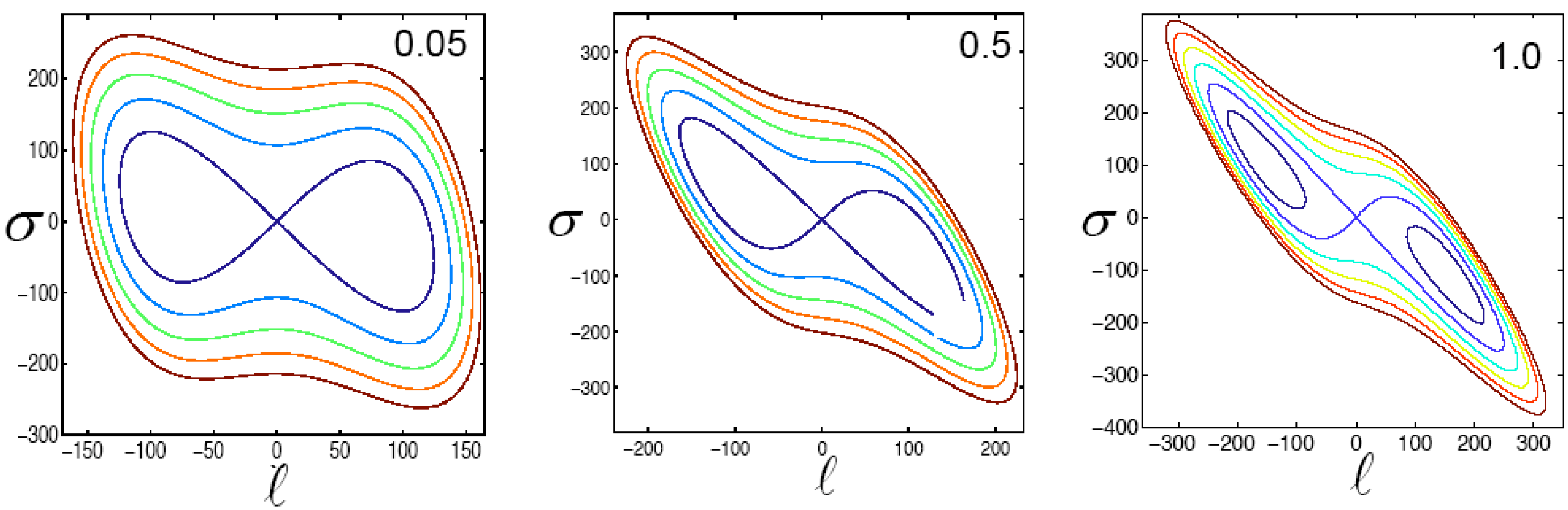
$$\tilde{\omega}_c = \omega_c + 2\lambda^\ddagger$$

$$\tilde{\epsilon} = \frac{\epsilon/M + 2\lambda^\ddagger(1 + \lambda^\ddagger/\omega_c)^2}{(1 + 2\lambda^\ddagger/\omega_c)^2} \longrightarrow_{\epsilon\to 0} \frac{2\omega^\ddagger(1 + \omega^\ddagger/\omega_c)^2}{(1 + 2\omega^\ddagger/\omega_c)^2}$$

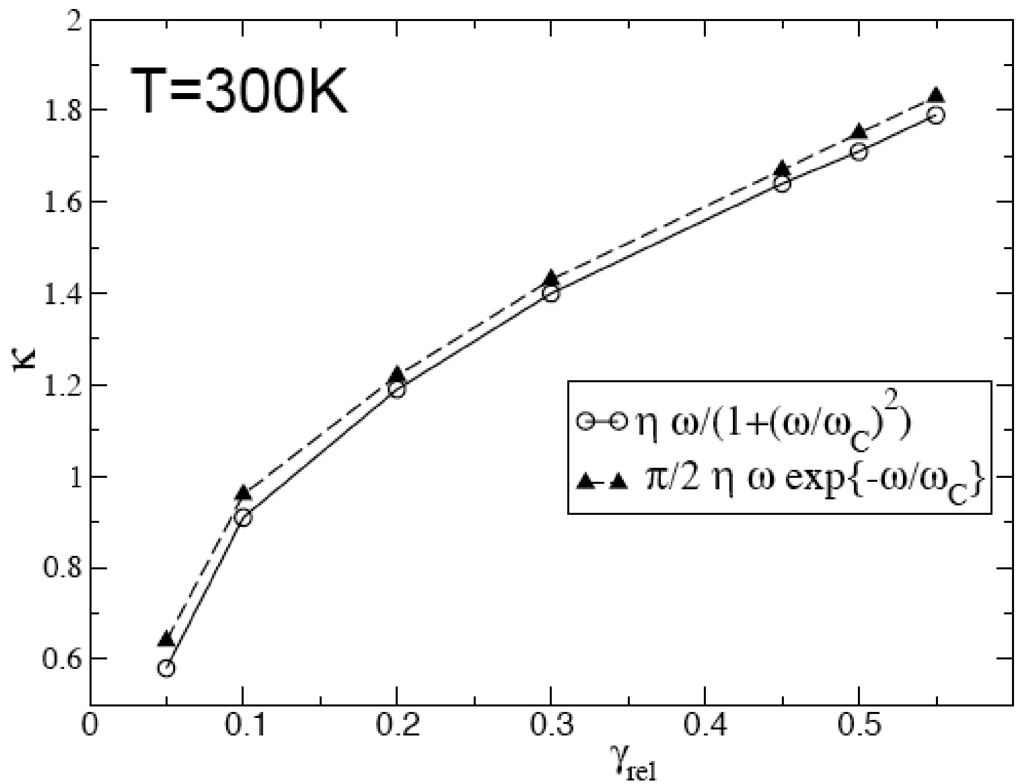
2-d Potential Surface in QME-CM

$$H = \frac{1}{2}(p_\ell^2 + p_\sigma^2 - \lambda^{\#2}\ell^2 + \omega_\sigma^2\sigma^2) + W_1(q(\ell,\sigma))$$

$$W(\ell,\sigma) = \frac{1}{2}(-\lambda^{\#}\ell^2 + \omega_\sigma^2\sigma^2) + \frac{\omega^{\#4}}{16E^{\#}}(u_{00}\ell + u_1\sigma)^4$$

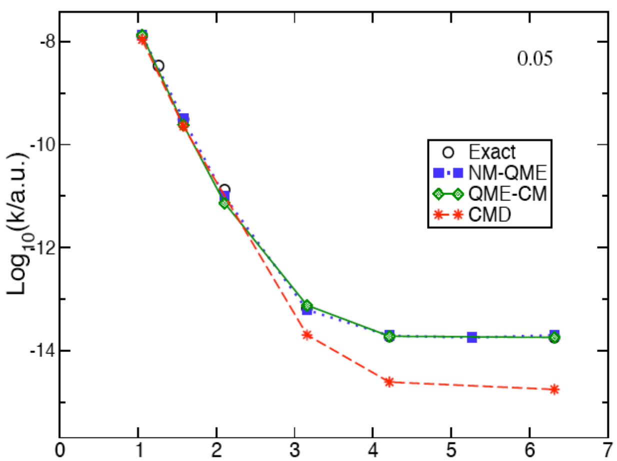


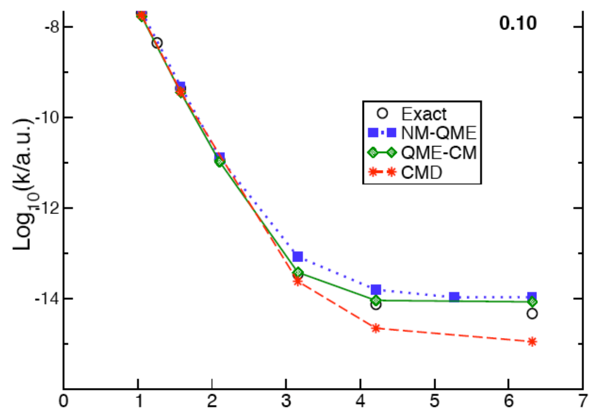
Drude vs. Ohmic Spectral Density

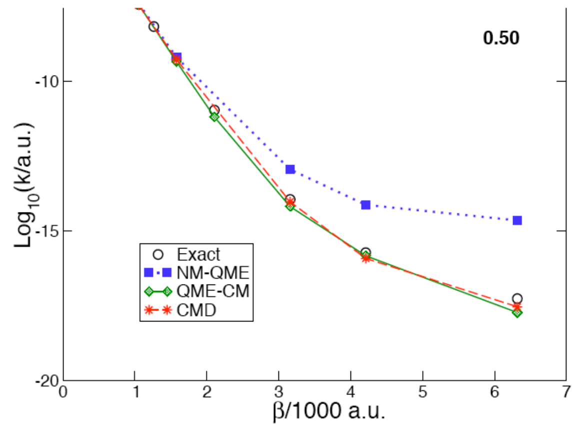


4. Results (DW1 parameters)

Barrier transmission vs. temperature for different frictions

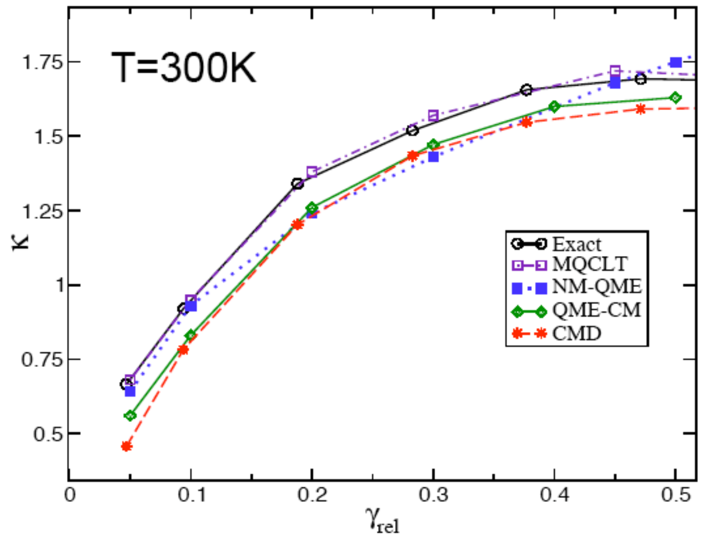


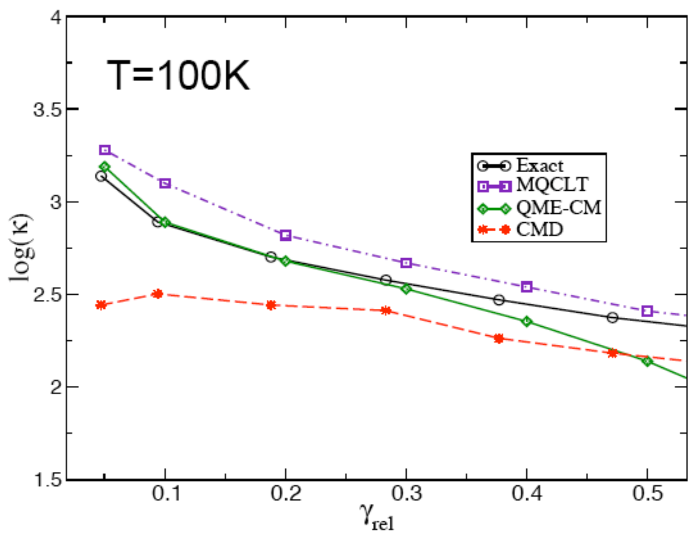




Low friction → Intermediate friction

Barrier transmission vs. friction: Kramers turnover?





Conclusions

•NME-CM extends the range of validity of QME from dimensionless frictions of 0.1 to 0.5

•The computational effort scales approximately as N^3 compared with the exponential scaling of path integration

•In contrast with methods based on classical dynamics, the NME-CM does exact quantum mechanics in the system degrees of freedom, and hence does not deteriorate at low T.

•NME-CM should find a useful niche for computing quantum rate constants at low temperature and intermediate friction

•Can the strategy be extended to dissipative dynamical processes other than barrier crossing? Can it be extended to stronger friction?

Results: Barrier Crossing in a Double Well

<u>NM-QME:</u>

✓Spectral density: Ohmic with exponential cut-off.

✓The potential: $W(q) = -\frac{m_0 \omega^{\#2}}{2} q^2 + \frac{m_0^2 \omega^{\#4}}{16 E^{\#}} q^4$

with parameters of DW1 [3].

✓Dimensionless coupling strength $\gamma_{\mathrm{rel}} = \varepsilon / m_0 \omega^{\#}$