Workshop Mini Project

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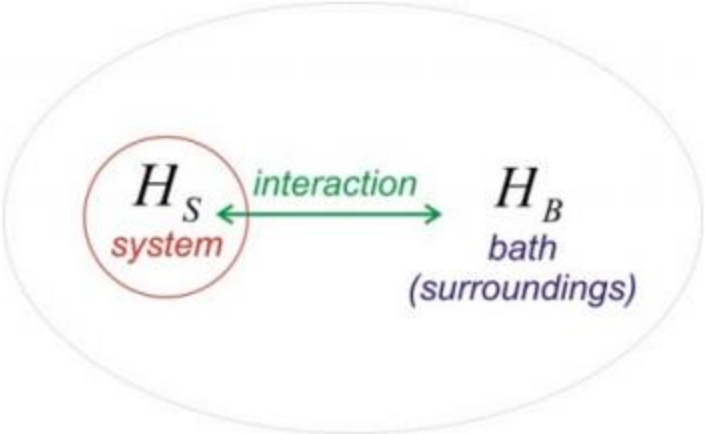


KC-RPMD

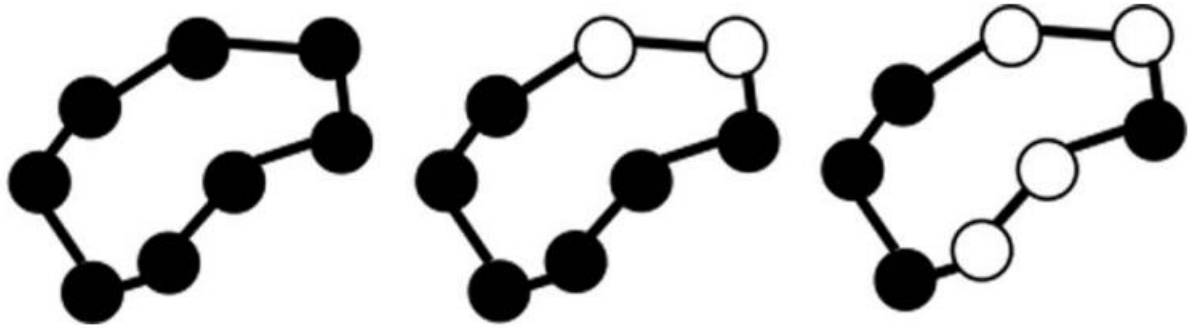


FIG. 1. A schematic illustration of ring-polymer configurations that exhibit either zero (left), one (center), or two (right) kink-pairs. Ring-polymer beads shown in white correspond to the electronic state $i^{(\alpha)} = 0$, whereas those in black correspond to $i^{(\alpha)} = 1$.

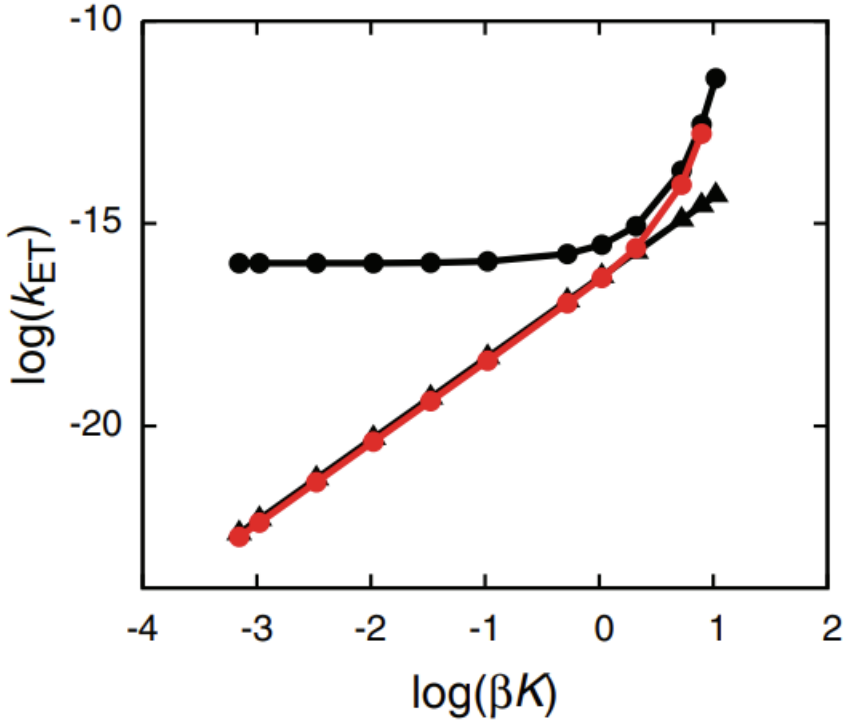
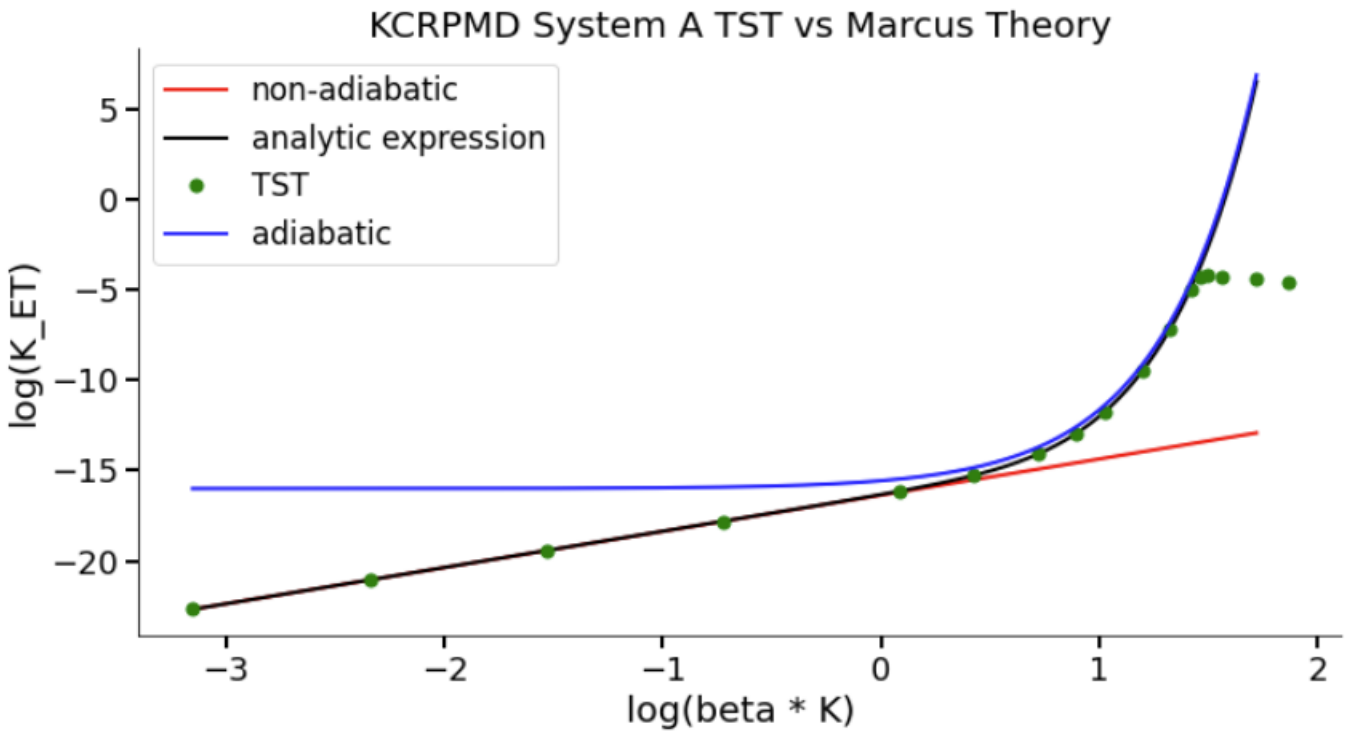
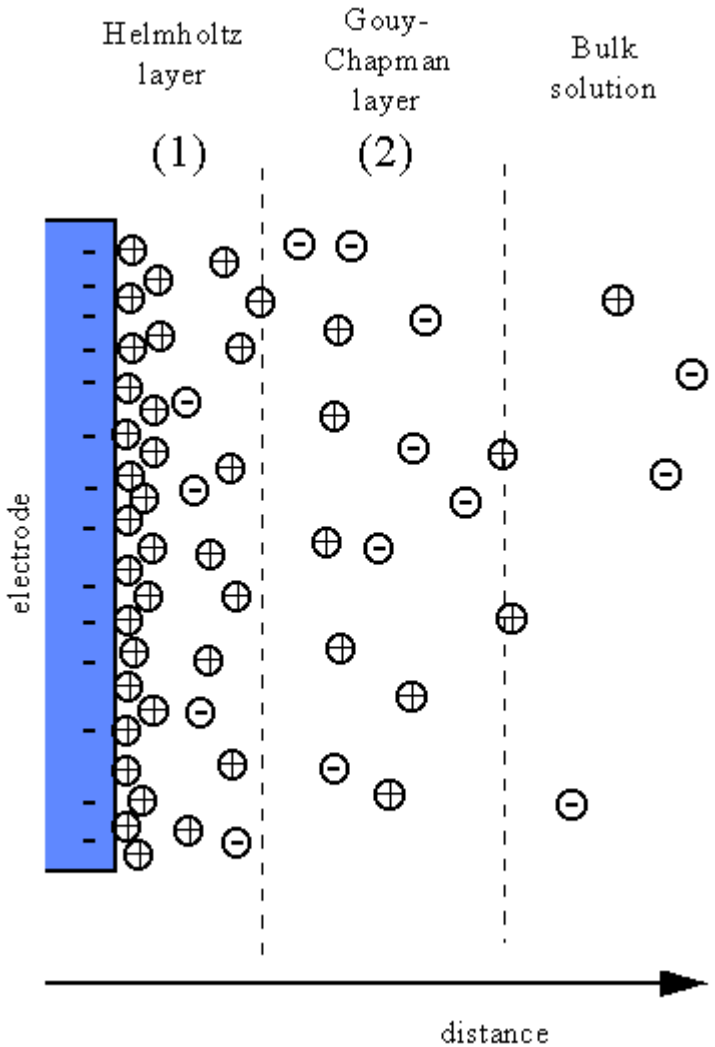
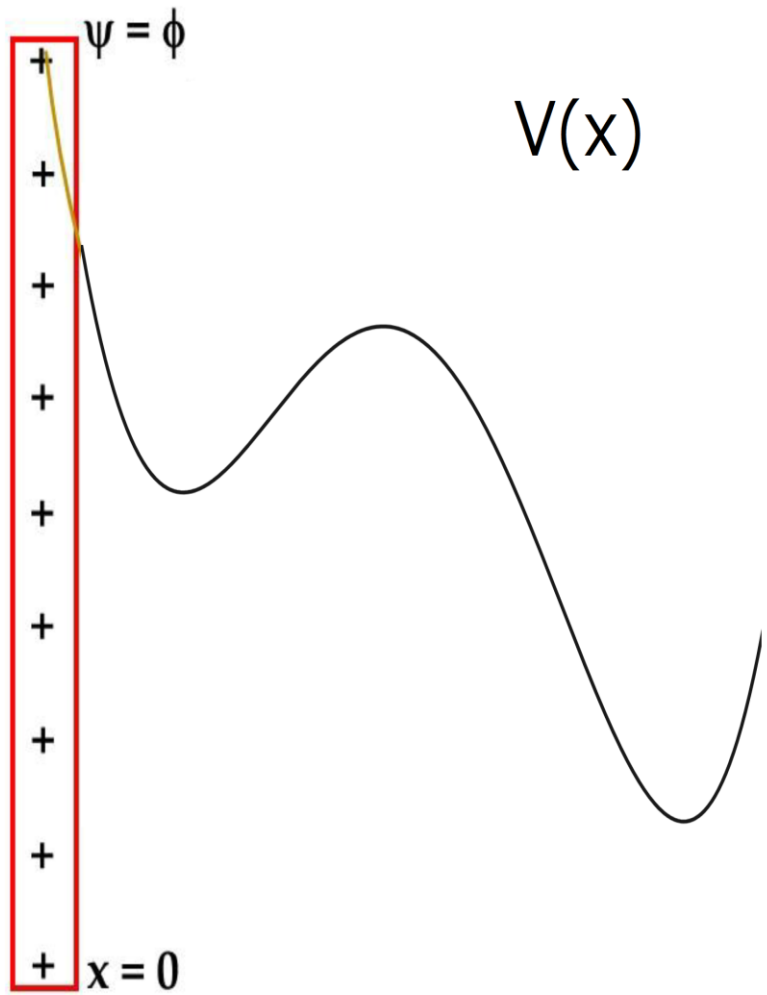


FIG. 5. ET reaction rate coefficients for System B with a classical description of the solvent coordinate obtained as a function of the diabatic coupling using KC-RPMD (red), the non-adiabatic rate expression in Eq. (63) (black triangles), and the adiabatic rate expression in Eq. (62) (black circles).

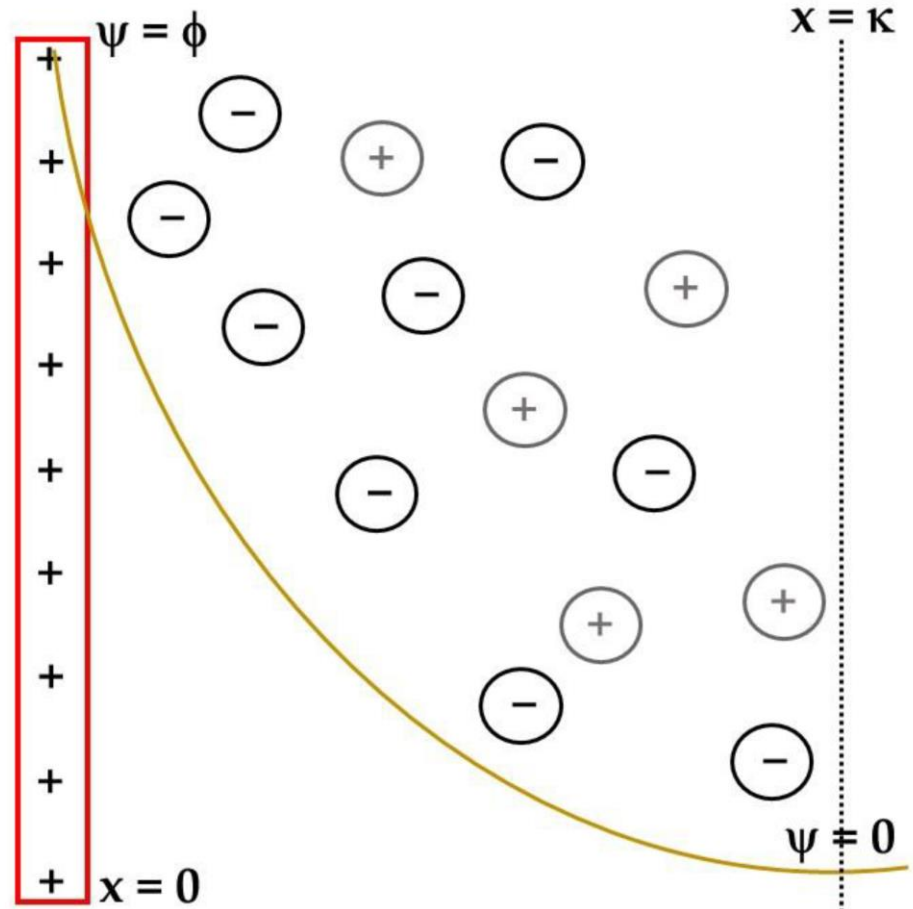


Next for KC-RPMD





V(x)



The Need To Benchmark

$$k_{\mathrm{ET}}^{\mathrm{ad}} = \frac{\omega_{\mathrm{s}}}{2\pi} \exp\left[-\beta G_{\mathrm{ad}}^{\ddagger}\right], \tag{62}$$

$$k_{\mathrm{ET}}^{\mathrm{nad}} = \frac{2\pi}{\hbar} |K|^2 \sqrt{\frac{\beta}{4\pi\lambda}} \exp\left[-\beta \frac{(\lambda + \Delta G^o)^2}{4\lambda}\right], \tag{63}$$

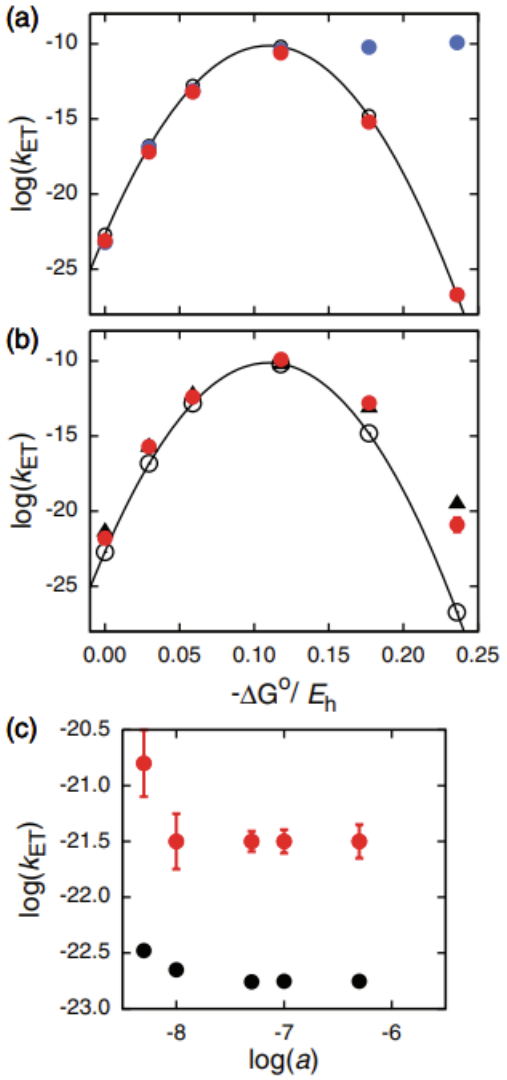


FIG. 3. (a) ET reaction rate coefficients for System B with a classical description of the solvent coordinate obtained as a function of ET driving force using KC-RPMD (red), classical MT (Eq. (63), black open circles), and position-representation RPMD (Ref. 23, blue). (b) The corresponding results for System B with a quantized description of the solvent coordinate obtained using KC-RPMD (red) and the golden-rule expression in Eq. (65) (black triangles). Results obtained using classical MT are also included for comparison (black open circles). (c) The convergence of the KC-RPMD reaction rate for symmetric ET with respect to the strength of kinetic constraint, a, including both classical (black) and quantized (red) descriptions of the solvent.

Hierarchical Equations of Motion

$$\mathrm{H} = \mathrm{H_S} + \mathrm{H_{SR}} + \mathrm{H_R}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + V_{\mathrm{S}}(\hat{q}) + \sum_j \left[\frac{\hat{p}_j^2}{2m_j} + \frac{m_j \omega_j^2}{2} \left(\hat{x}_j - \frac{c_j \hat{q}}{m_j \omega_j^2} \right)^2 \right], \qquad (2.7)$$

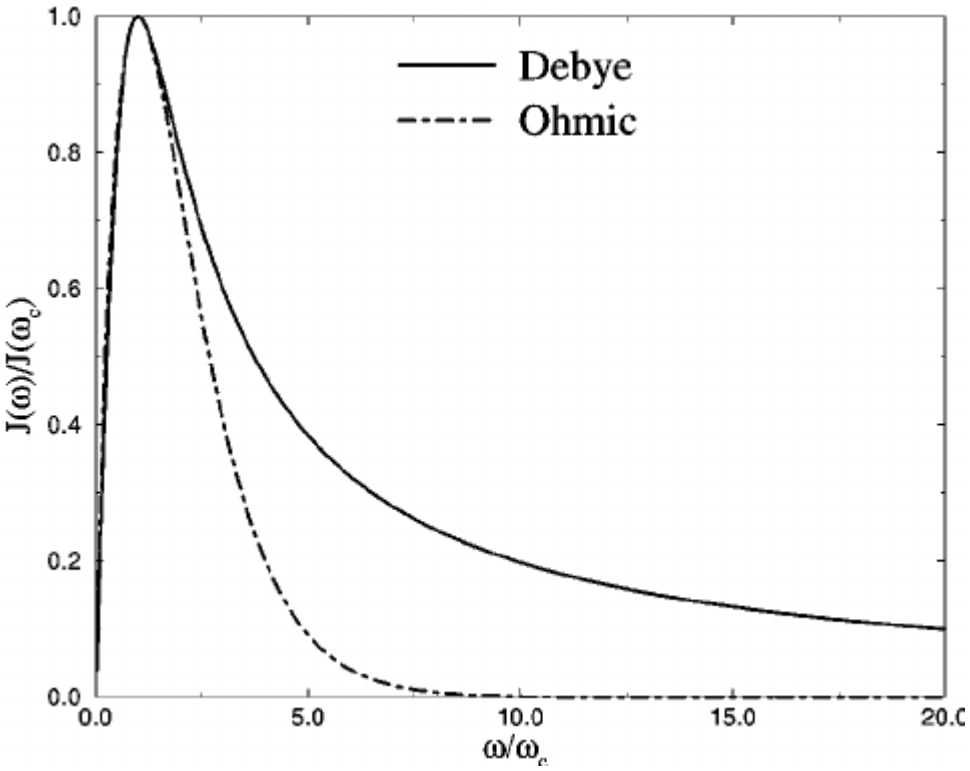
$$\frac{\partial}{\partial \mathrm{t}} \hat{\rho}(\mathrm{t}) = -\frac{\mathrm{i}}{\hbar} [\mathrm{H_S}, \hat{\rho}(\mathrm{t})] - \frac{\mathrm{i}}{\hbar} \mathrm{tr}\{[\mathrm{H_{SR}}, \widehat{\mathrm{W}}(\mathrm{t})]\}$$

Hierarchical Equations of Motion

$$J_n(\omega) = \frac{\pi}{2}\sum_{b=0}^{N_n-1}\frac{f_{b,n}^2}{\omega_{b,n}}\delta(\omega-\omega_{b,n})$$

$$J_n(\omega) = \frac{\eta\gamma\omega^2}{\omega^2+\gamma^2}$$

$$C(t>0) = \sum_{k=0}^{\infty} c_k \exp(-\gamma_k t)$$



$$\dot{\rho}_n = -i[H,\rho_n] - \sum_{m=0}^{M-1}\left(\sum_{k=0}^{\infty} n_{mk}\gamma_{mk}\right)\rho_n + \rho_n^{(+)} + \rho_n^{(-)} + T_n$$

Note on Rate Constants (first order kinetics)

$$\dot{P}_0(t) = -k_f P_0(t) + k_b P_1(t)$$

$$\dot{P}_1(t) = k_f P_0(t) - k_b P_1(t)$$

- Detailed balance, equilibrium reached with long enough times

$$\lim_{t\to\infty} \dot{P}_0(t) = -k_f\langle P_0\rangle + k_b\langle P_1\rangle = 0$$

Solving Rate constants with HEOM

- Set Electron population on reactant basin and allow bath to thermalize.
- Once thermalized, allow electrons to decay to steady state equilibrium.

```
T = 300.
beta = 1 / (T * 3.16681156345e-6)

V = 0.001 / beta
E0 = 10.0 / beta
lam = 10. / beta
gam = 0.1 / beta

#print(2 * 3.1415 * V**2 * (beta / (4 * 3.1415 * lam))**0.5 * np.exp(-beta * (lam - E0)**2 / (4 * lam)))

delt = 0.5
nsteps = 500000
step_switch = 125000

# Hamiltonian
Ham1 = CMATRIX(2,2)
Ham1.set(0, 0, 0.5 * E0);  Ham1.set(0, 1, 0.);
Ham1.set(1, 0, 0.);   Ham1.set(1, 1, -0.5 * E0)
Ham1.scale(-1,-1, (1.0+0.0j))

Ham2 = CMATRIX(2,2)
Ham2.set(0, 0, 0.5 * E0);  Ham2.set(0, 1, V);
Ham2.set(1, 0, V);   Ham2.set(1, 1, -0.5 * E0)
Ham2.scale(-1,-1, (1.0+0.0j))

# Initial density matrix
rho_init = CMATRIX(2,2); rho_init.set(0, 0, 1.0+0.0j) # starting state = initial state
```

```
#============== Propagation =============


start = time.time()
for step in range(params["nsteps"]):

    #================ Saving and printout ==================
    # scaled -> raw
    transform_adm(rho, rho_scaled, aux_memory, params, -1)

    # Save the variables
    save.save_heom_data(_savers, step, print_freq, params, aux_memory["rho_unpacked"])
```

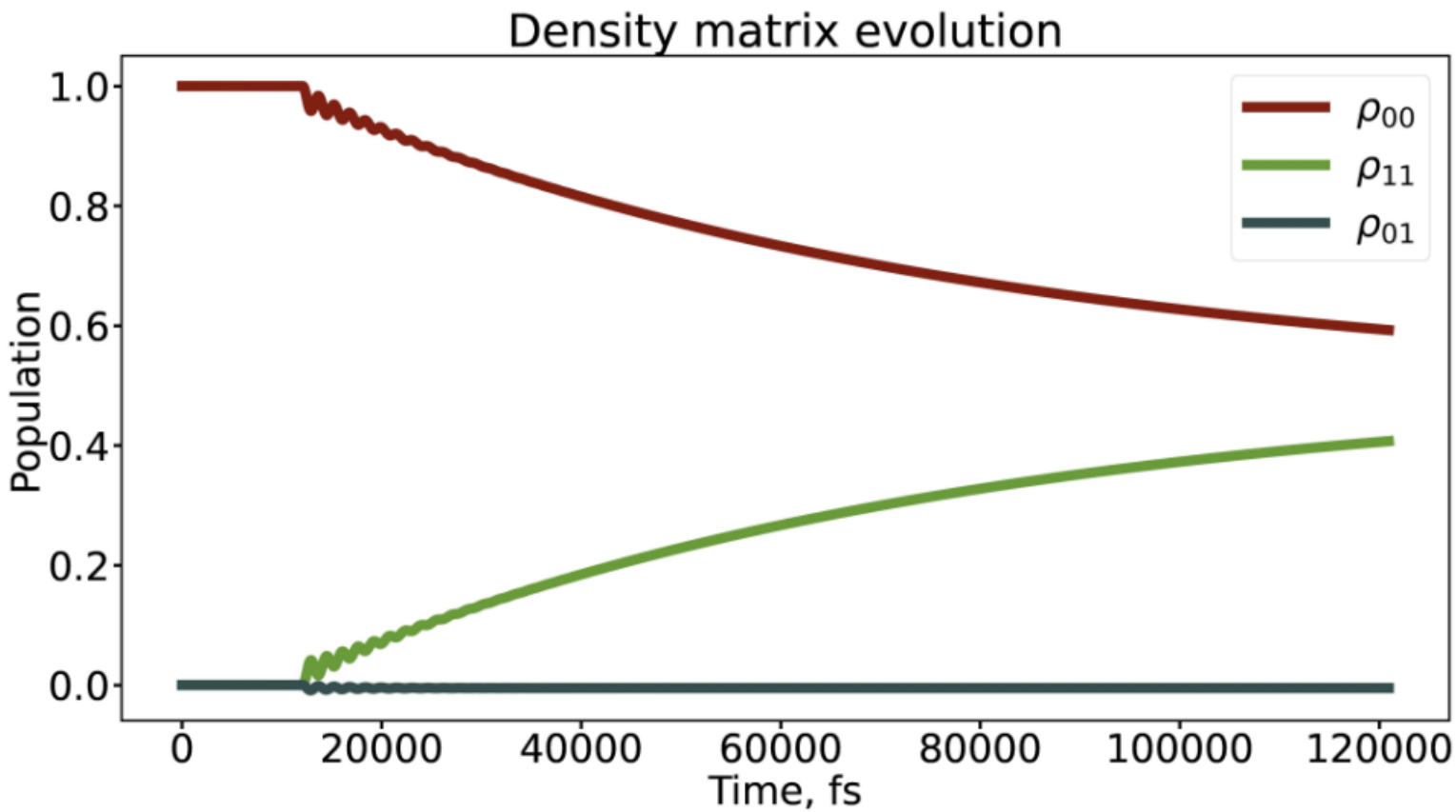


Figure 1. HEOM solution to density matrix following brief thermalization period. Parameters were set to $T = 300\ K$, $E_0 = 0$, $V = 0.01 * \beta$, $\lambda = 0.01 * \beta$, and $\gamma = 0.01 * \beta$. The convergence parameters were set to $L = 10$, and $K = 0$.

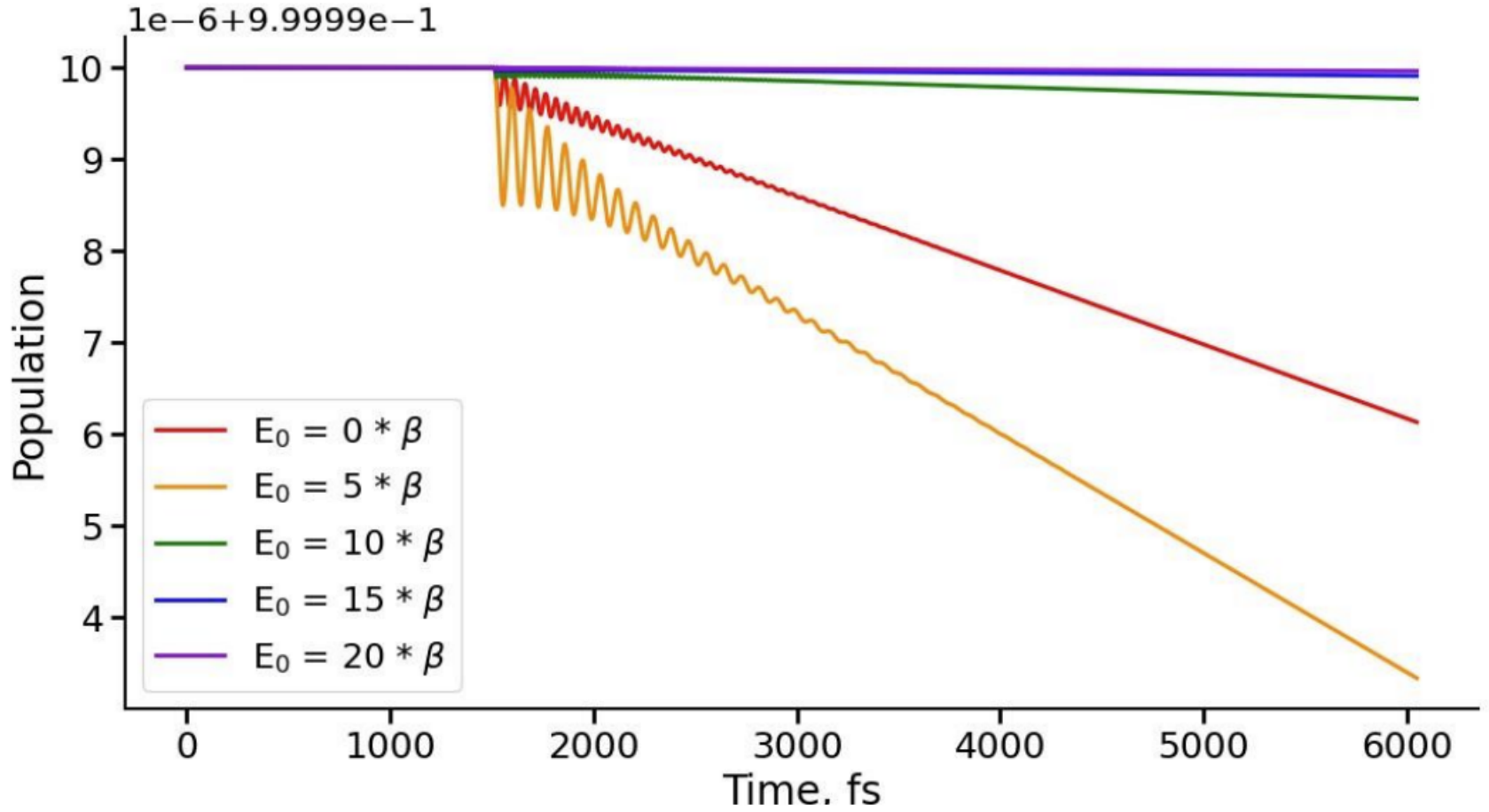


Figure 2. HEOM reactant state populations after a brief (yet relatively short) thermalization period as a function of driving force. Parameters were set to $T = 300\ K$, $V = 0.001 * \beta$, $\lambda = 10 * \beta$, and $\gamma = 0.1 * \beta$. The convergence parameters were set to $L = 1$, and $K = 32$.

Thanks