Open-chain Path-integral Method to Fermi's Golden Rule Rate

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Fermi's Golden Rule Charge Transfer Rates

Fermi's golden rule (FGR) rate is a quantum rate for a quantum transition like charge transfer (CT) population transfer, whose system Hamiltonian can be given by

$$\hat{H} = \hat{H}_D|D\rangle\langle D| + \hat{H}_A|A\rangle\langle A| + \hat{\Gamma}_{DA}|D\rangle\langle A| + \hat{\Gamma}_{AD}|A\rangle\langle D|$$

where $\hat{H}_{D/A} = \hat{\mathbf{P}}^2/2 + V_{D/A}(\hat{\mathbf{R}})$ is donor/acceptor Hamiltonian, $\hat{\mathbf{P}} = \{P_j|j=1,\cdots,N\}$ and $\hat{\mathbf{R}} = \{R_j|j=1,\cdots,N\}$ serves as momenta and positions of a system with nuclear degrees of freedom of N, $V_{D/A}$ serves as donor/acceptor state PES, under Condon approximation, diabatic coupling is a constant, $\hat{\Gamma}_{DA} = \hat{\Gamma}_{AD} = \Gamma$, whose corresponding Fermi's Golden rule rate coefficient is

$$k = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t C_{DA}(t)$$

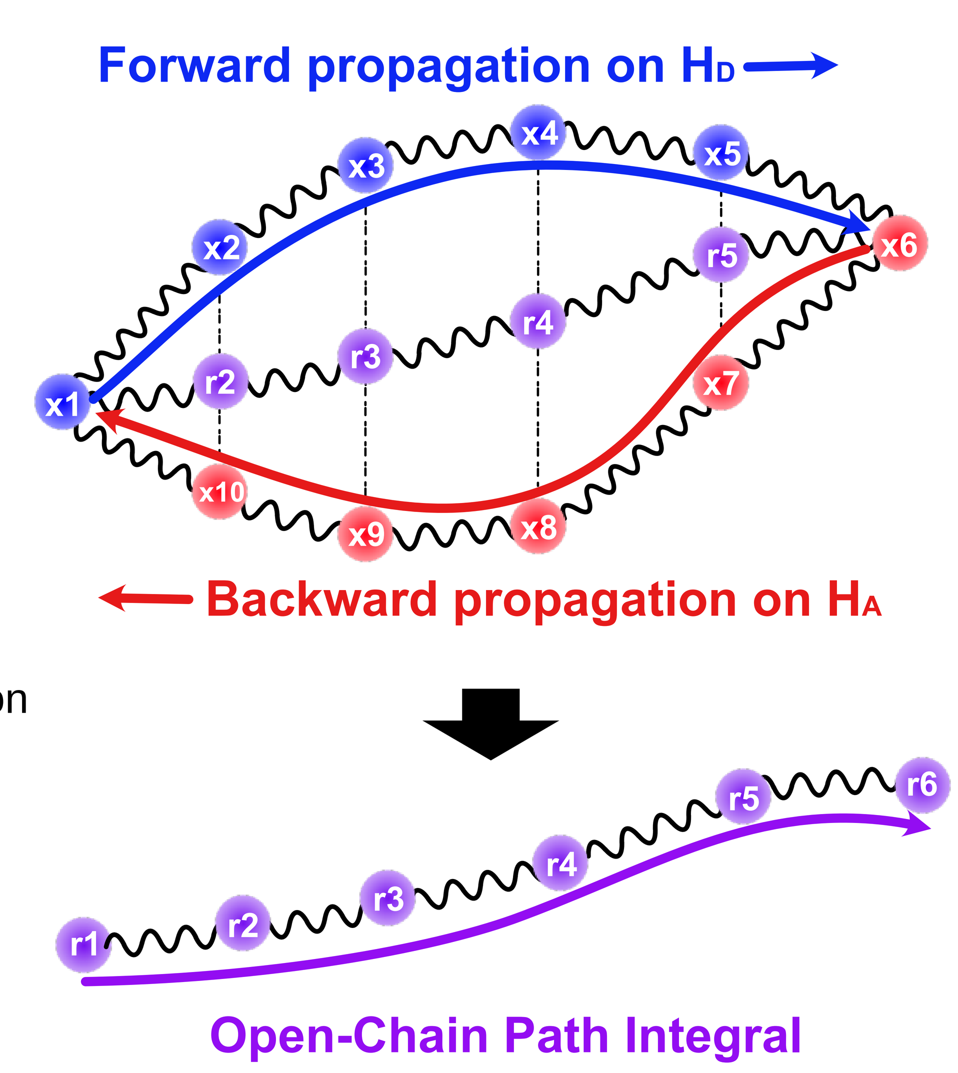
where quantum time correlation function is $C_{DA}(t) = C^{\dagger}_{AD}(t) = \frac{1}{Z_D}\mathrm{Tr}_N\left[e^{-\beta\hat{H}_D}e^{i\hat{H}_D t/\hbar}\hat{\Gamma}_{DA}e^{-i\hat{H}_A t/\hbar}\hat{\Gamma}_{AD}\right]$ and Tr_N is trace over nuclear degrees of freedom.
It can be converted to ***symmetrized time correlation function (SCF)*** via $\tau_c = t - i\beta\hbar/2$ and obtain the 2-state SCF

$$\boxed{G_{AD}(t) = \frac{1}{Z_D}\mathrm{Tr}_N\left[\hat{\Gamma}_{DA}e^{i\hat{H}_A\tau_c^*/\hbar}\hat{\Gamma}_{AD}e^{-i\hat{H}_D\tau_c/\hbar}\right]}$$

This can be sampled by open-chain path-integral (OCPI) approach.

Open-Chain Path Integral Method

Figure #1 Schematic of Open-chain Path-integral Approach: From ring polymer to open chain



The 2-state SCF of 1-dimensional system can be cast in position basis

$$G_{AD}(t) = \int \mathrm{d}x\,\mathrm{d}x'\Gamma_{DA}(x)\left\langle x\left|e^{i\hat{H}_A\tau_c^*/\hbar}\right|x'\right\rangle$$
$$\times\Gamma_{AD}(x')\left\langle x'\left|e^{-i\hat{H}_D\tau_c/\hbar}\right|x\right\rangle,$$

where we can apply Trotter splitting, Condon Approximation, and linearization variable Transformation as below

$$r^{(1)} = x^{(1)},\quad r^{(P+1)} = x^{(P+1)},$$
$$r^{(\alpha)} = \frac{1}{2}\left[x^{(\alpha)} + x^{(2P+2-\alpha)}\right],\qquad (\alpha = 2,\cdots,P),$$
$$s^{(\alpha)} = x^{(\alpha)} - x^{(2P+2-\alpha)},\qquad (\alpha = 2,\cdots,P).$$

and $\{x^{(\alpha)}|\alpha = 1,\cdots,2P\}$ is the bead positions.

In linearized symmetrized correlation function integrate over the path-difference variables and employ the enhanced sampling approach to get OCPI symmetrized correlation function given by

$$G_{AD}(t) = \Gamma^2\frac{\tilde{Z}_{\mathrm{av}}}{Z_D}\left\langle e^{i\Phi(\mathbf{r})}\frac{e^{-\beta W(\mathbf{r})}}{e^{-\beta W_{\mathrm{av}}(\mathbf{r})}}\right\rangle_{\mathrm{av}}.\qquad Z_D = \mathrm{Tr}[\exp(-\beta\hat{H}_D)]$$

Here, < >av is canonical ensemble average of effective Hamiltonian with averaged PES partition, interbead frequency is $\omega_P = \sqrt{P}/|\tau_c|$, the effective Hamiltonian is

$$\tilde{H}_{av} = \frac{\mathbf{p}^2}{2} + \sum_{\alpha=1}^{P}\frac{1}{2}m\omega_P^2(r^{(\alpha+1)} - r^{(\alpha)})^2 + \frac{1}{P}\left[\sum_{\alpha=2}^{P}\overline{V}(r^{(\alpha)}) + \frac{1}{2}\overline{V}(r^{(1)}) + \frac{1}{2}\overline{V}(r^{(P+1)})\right] + \frac{1}{2\beta}\left[\mathbf{K}(\mathbf{r})^T\mathbf{M}^{-1}(\mathbf{r}')\mathbf{K}(\mathbf{r}) + \ln(\det[\mathbf{M}(\mathbf{r}')])\right]_{\mathrm{av}}$$

- quantum phase factor $\Phi(\mathbf{r}) = \frac{t}{P\hbar}\left[\sum_{\alpha=2}^{P}\Delta V(r^{(\alpha)}) + \frac{1}{2}\Delta V(r^{(1)}) + \frac{1}{2}\Delta V(r^{(P+1)})\right],$
- complex bead average weight $W(\mathbf{r}) = \frac{1}{2\beta}\left[\mathbf{K}(\mathbf{r})^T\mathbf{M}^{-1}(\mathbf{r}')\mathbf{K}(\mathbf{r}) + \ln(\det[\mathbf{M}(\mathbf{r}')])\right]_{\mathrm{complex}},$
- real bead average weight $W_{\mathrm{av}}(\mathbf{r}) = \frac{1}{2\beta}\left[\mathbf{K}(\mathbf{r})^T\mathbf{M}^{-1}(\mathbf{r}')\mathbf{K}(\mathbf{r}) + \ln(\det[\mathbf{M}(\mathbf{r}')])\right]_{\mathrm{av}},$
- matrix elements $M_{\alpha\alpha'}(\mathbf{r}') = \left[2A + \frac{\beta}{4P}\overline{V}''(r^{(\alpha)}) - \frac{it}{4P\hbar}\Delta V''(r^{(\alpha)})\right]\delta_{\alpha\alpha'} - A\delta_{\alpha+1,\alpha'} - A\delta_{\alpha,\alpha'+1},\quad (\alpha,\alpha' = 2,\ldots,P)$

$$K_\alpha(\mathbf{r}) = \gamma\left(2r^{(\alpha)} - r^{(\alpha-1)} - r^{(\alpha+1)}\right) - \frac{t}{P\hbar}\overline{V}'(r^{(\alpha)}) - \frac{i\beta}{4P}\Delta V'(r^{(\alpha)}),\quad (\alpha = 2,\ldots,P),$$

where $A = \frac{mP\beta}{4|\tau_c|^2},\qquad \gamma = \frac{mPt}{\hbar|\tau_c|^2}$

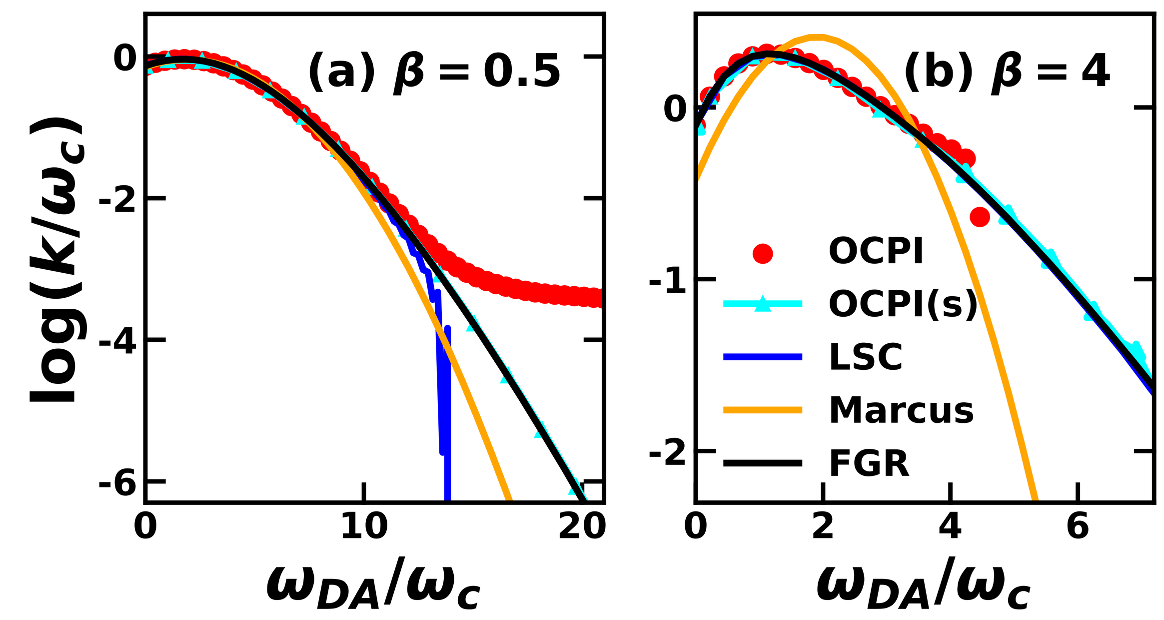
Model Hamiltonian employed here is a 19-mode spin-boson Hamiltonian

$$\hat{H} = \Gamma\hat{\sigma}_x - \frac{\Delta E}{2}\hat{\sigma}_z + \sum_{j=1}^{N}\left(\frac{\hat{P}_j}{2} + \frac{1}{2}\omega_j^2\hat{R}_j^2 - c_j\hat{R}_j\hat{\sigma}_z\right)$$

where $\hat{\sigma}_z = |D\rangle\langle D| - |A\rangle\langle A|$, $\hat{\sigma}_x = |D\rangle\langle A| + |A\rangle\langle D|$, $\Delta E = -\hbar\omega_{DA}$ is energy gap between donor and acceptor state, Γ serves as diabatic state coupling coefficient, and $\{\omega_j, c_j, \hat{R}_j, \hat{P}_j|j = 1,\cdots,N\}$ are normal mode frequencies, vibronic couplings, positions and momenta operator of the j-th mode.

OCPI Gives Accurate FGR CT Rates

Figure #2 FGR Rates



- ***OCPI method can reproduce the analytical FGR CT rate constant of the model system***
- *At **high** temperature, OCPI results agrees with the exact CT rates within $10\omega_c$ without smoothing and $20\omega_c$ with smoothing.*
- *At **low** temperature, OCPI can capture **NQE** with and without smoothing.*

Figure #3 Sampled SCF

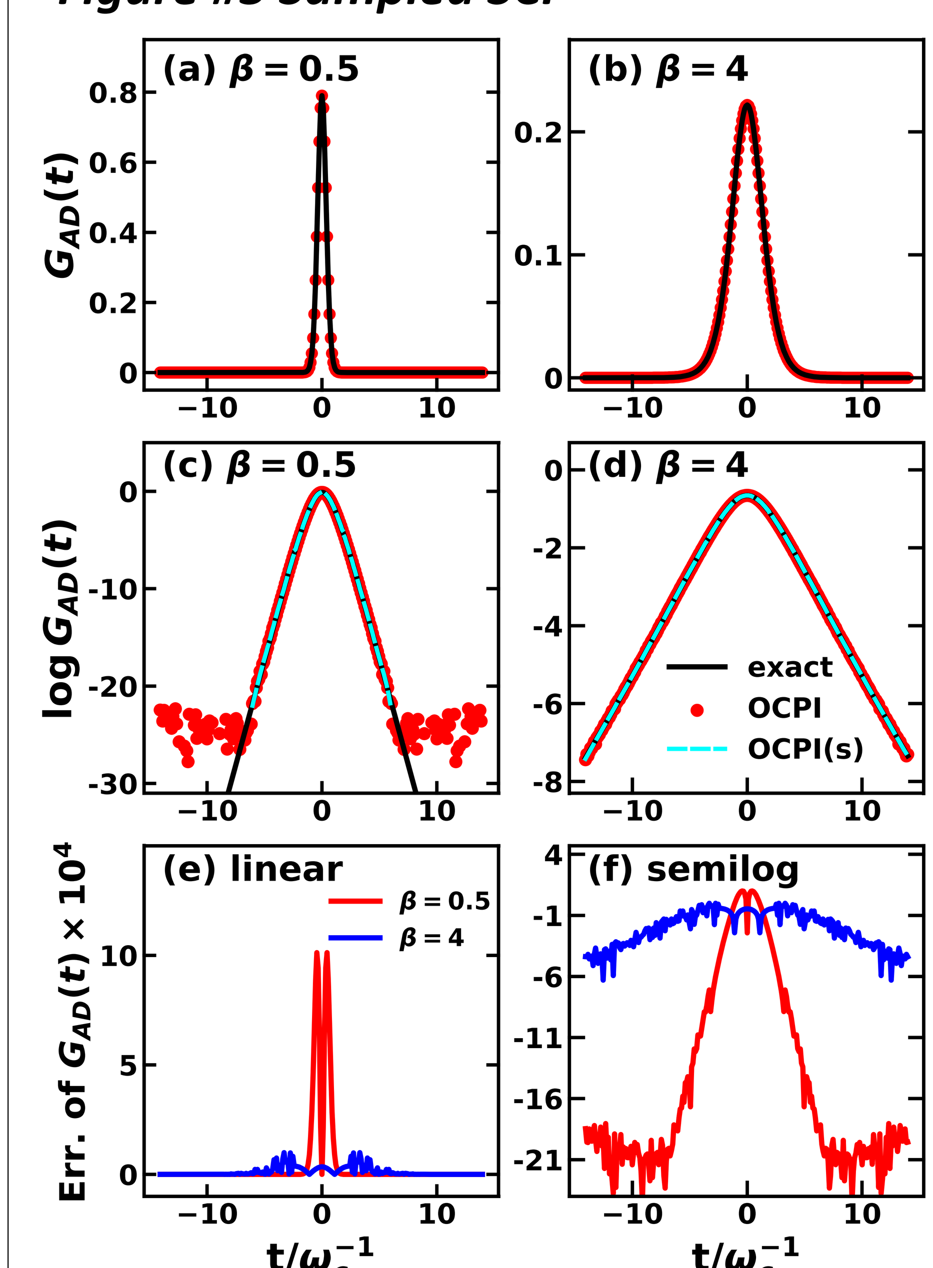
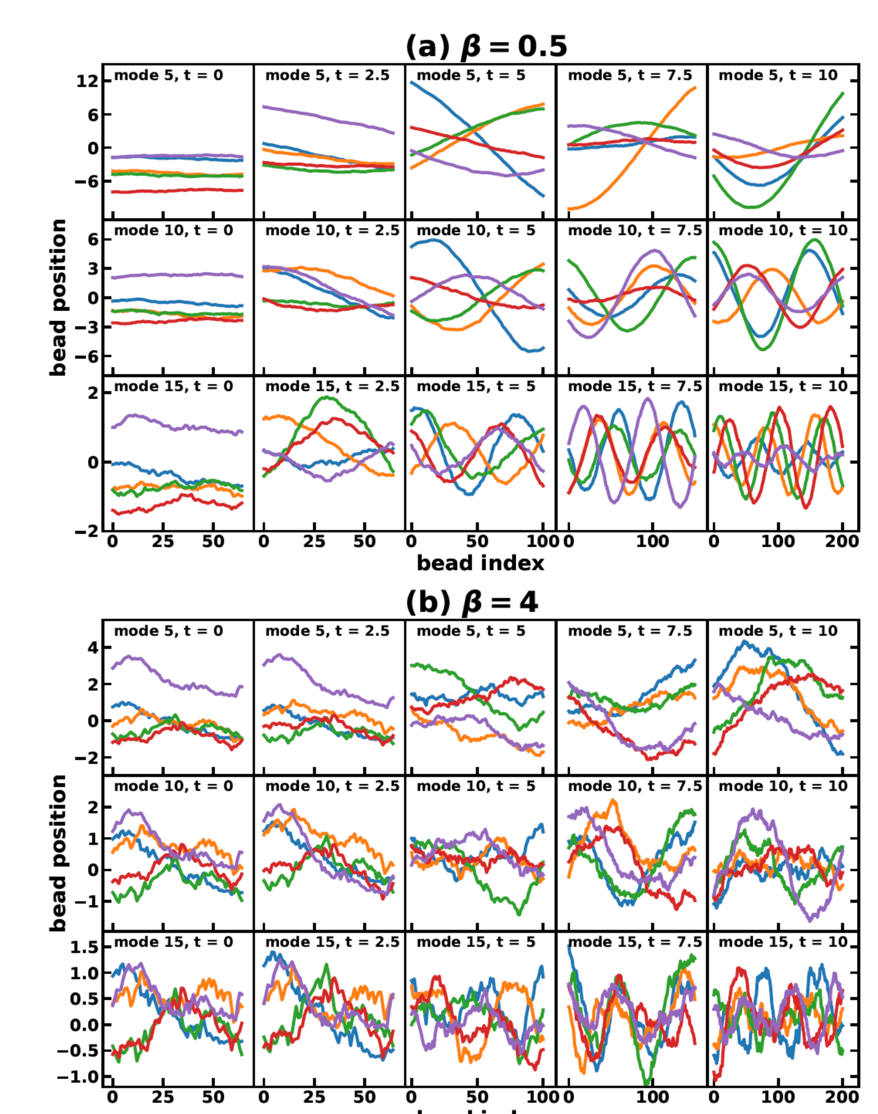
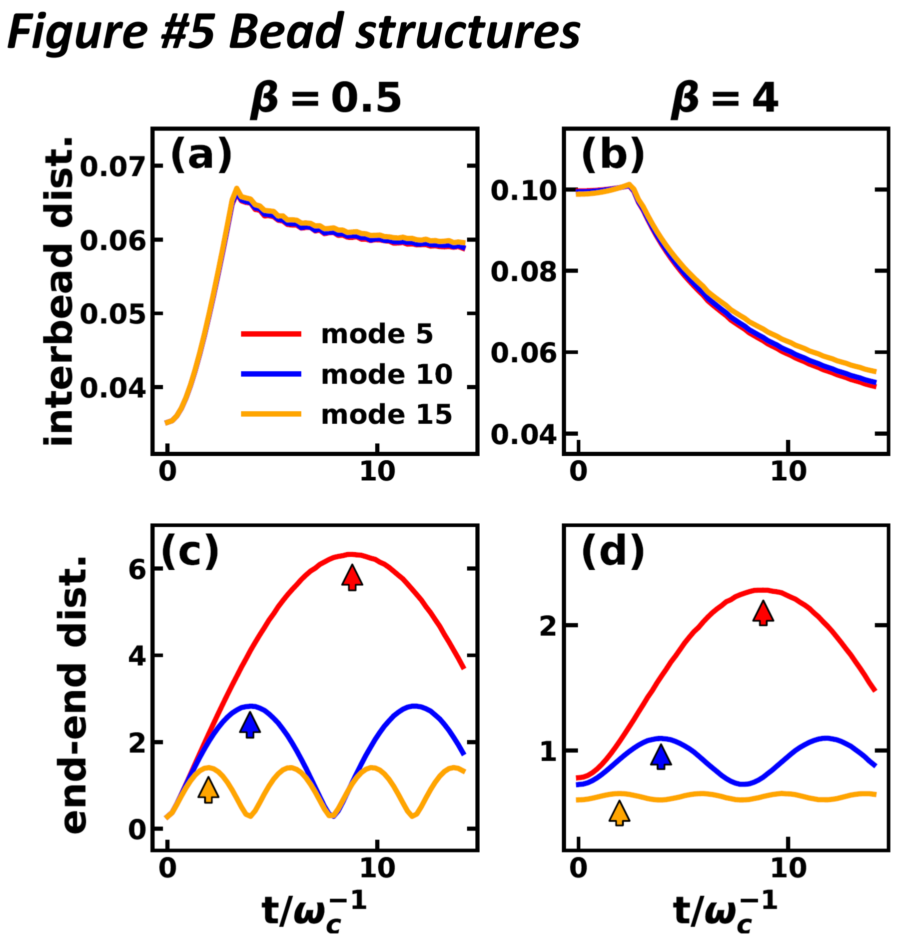


Figure #4 Sampled Configurations



- *OCPI can produce very **accurate** SCF*
- *The absolute sampling errors of SCF utilizing the OCPI method is small!*
  - ***less than 0.001** at high temperature*
  - ***less than 0.0001** at low temperature*
- ***Adding** smooth to the central part can further improve FGR CT rate constant.*

Figure #5 Bead structures



- *The end-to-end distance clearly exhibits **the real-time dynamics.***
- *The **first bead** of the open chain corresponds to **time 0; the last bead** of the open chain corresponds to the **time t.***
- *Intermediate beads follow a **chronological order** in-between time 0 and t.*

References
[1] J.R. Cendagorta, Z. Bačić, and M.E. Tuckerman, *J. Chem. Phys.* **148**(10), 102340 (2018).
[2] Z. Liu, W. Xu, M.E. Tuckerman, and X. Sun, *J. Chem. Phys.* **157**(11), 114111 (2022).

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