Whaley group meeting talk

Liwen Ko

09/17/2024

Outline

- Tutorial on input-output relation (board, 30 min)
- Analyzing optical signals (board, 3 min)
- Normal-ordered expansion of the reduced system state (slides, 5 min)
- Electron transfer assisted by off-resonant underdamped vibrations (slides, 7 min)
- Some open questions. My disorganized and speculative thoughts (board, 7 min)
- Conclusion (slides, 3 min)

Normal-ordered expansion for the reduced system state

Conventional time-ordered

$$\mathcal{L}(t) = [-a(t)L^\dagger + a^\dagger(t)L, \bullet]$$

$$\begin{aligned}\rho_{\mathrm{sys}}(t) = \mathrm{Tr}_{\mathrm{field}}\Big(& e^{\mathcal{K}' t}\rho_{\mathrm{tot}}(0) \\ &+ \int_0^t dt_1\, e^{\mathcal{K}'(t-t_1)}\mathcal{L}(t_1)e^{\mathcal{K}'(t_1)}\rho_{\mathrm{tot}}(0) \\ &+ \int_0^t dt_2 \int_0^{t_2} dt_1\, e^{\mathcal{K}'(t-t_2)}\mathcal{L}(t_2)e^{\mathcal{K}'(t_2-t_1)}\mathcal{L}(t_1)e^{\mathcal{K}'(t_1)}\rho_{\mathrm{tot}}(0) \\ &+ \cdots\Big).\end{aligned}$$

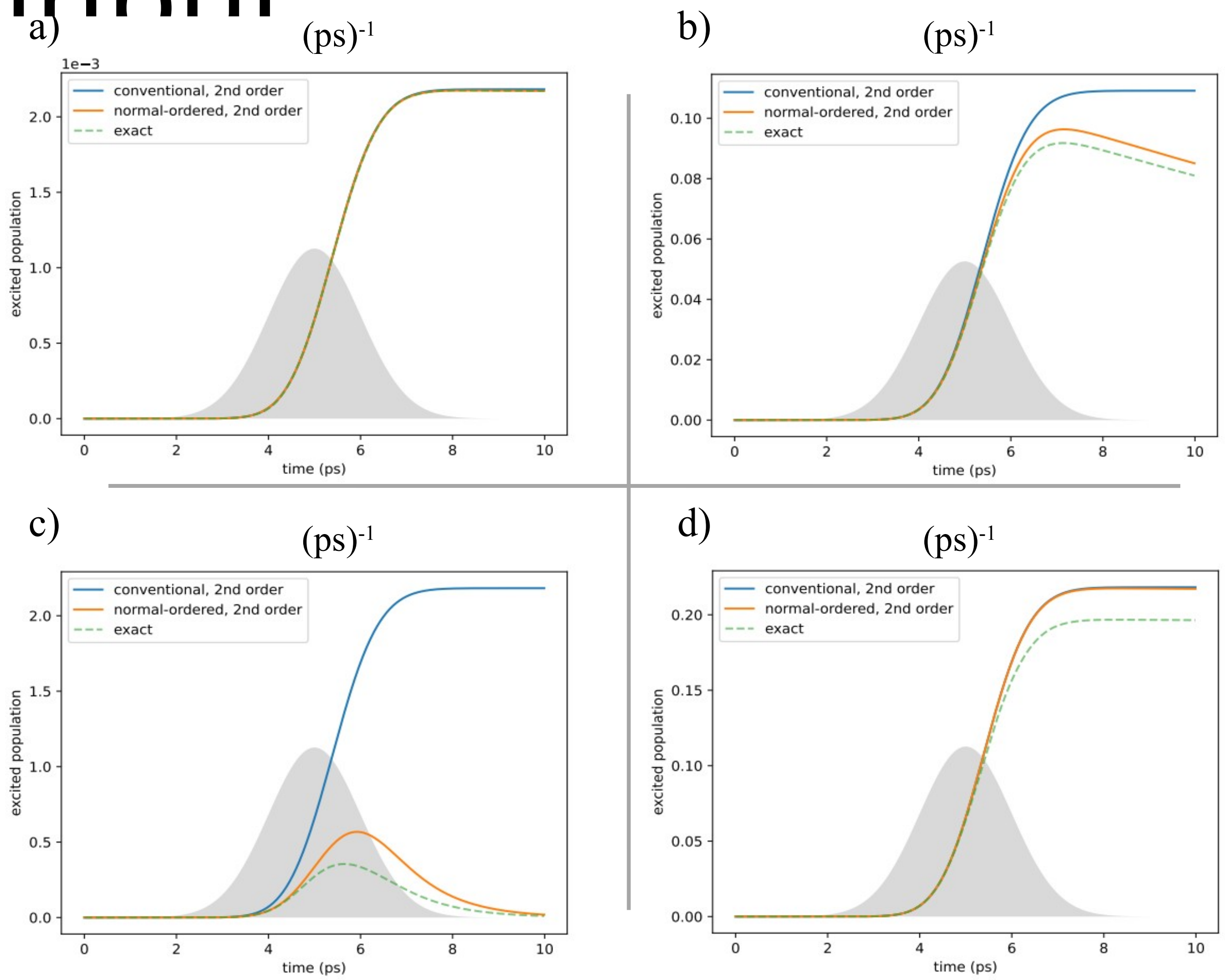
$$\mathcal{K}' = -i[H_{\mathrm{sys}}, \bullet]$$

Normal-ordered

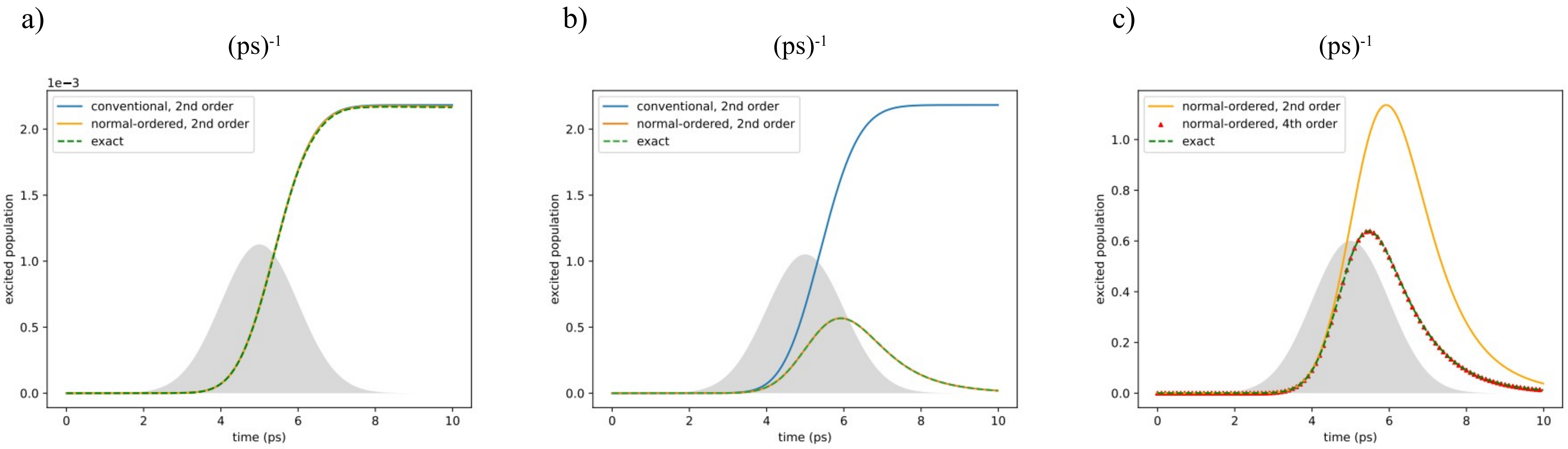
$$\mathcal{K} = -i[H_{\mathrm{sys}}, \bullet] - \frac{1}{2}\{L^\dagger L \bullet\} + L \bullet L^\dagger$$

$$\begin{aligned}\rho_{\mathrm{sys}}(t) = \mathrm{Tr}_{\mathrm{field}}\hat{\mathcal{N}}\Bigg(& e^{\mathcal{K}t}\rho_{\mathrm{tot}}(0) \\ &+ \int_0^t dt_1\, e^{\mathcal{K}(t-t_1)}\mathcal{L}(t_1)e^{\mathcal{K}t_1}\rho_{\mathrm{tot}}(0) \\ &+ \int_0^t dt_2 \int_0^{t_2} dt_1\, e^{\mathcal{K}(t-t_2)}\mathcal{L}(t_2)e^{\mathcal{K}(t_2-t_1)}\mathcal{L}(t_1)e^{\mathcal{K}(t_1)}\rho_{\mathrm{tot}}(0) \\ &+ \cdots\Bigg).\end{aligned}$$

Normal-ordered expansion for the reduced system state – coherent state input



Normal-ordered expansion for the reduced system state – m-photon Fock state input



Truncates at 2m-th order ☾ exact expression

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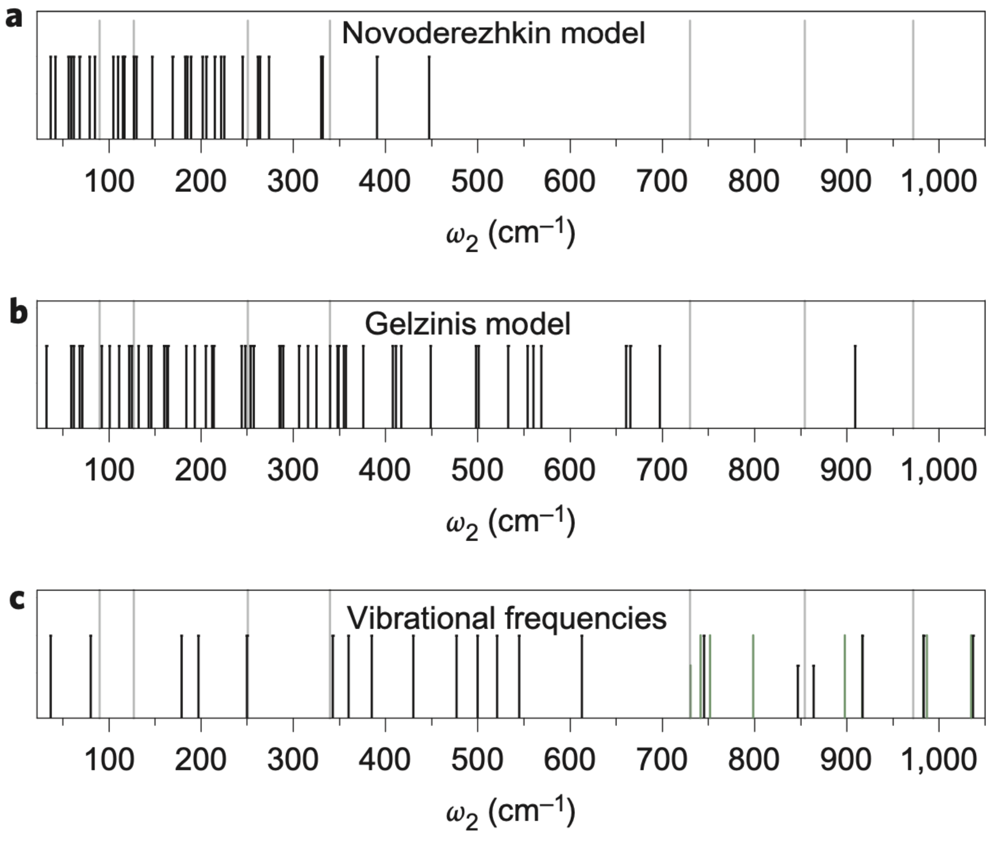
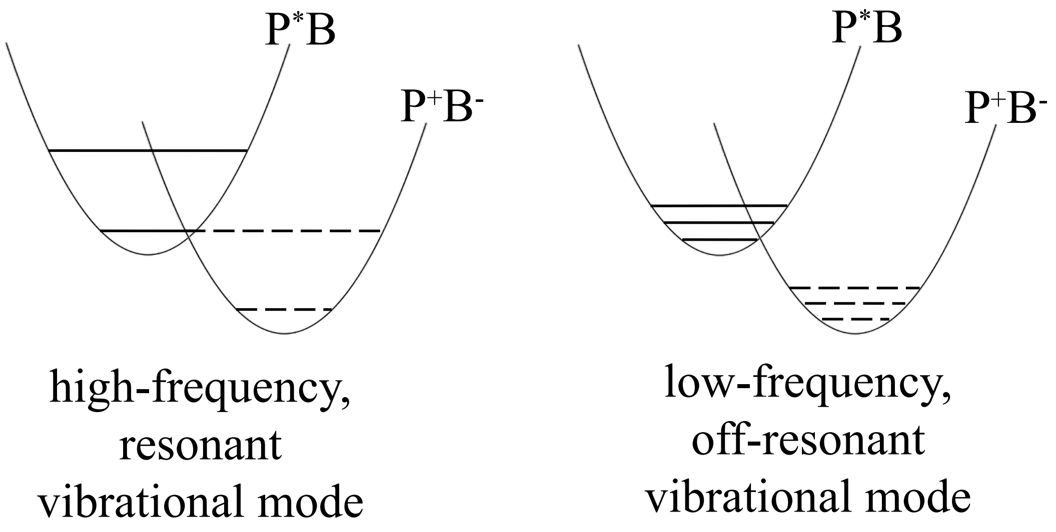
Electron transfer assisted by underdamped nuclear vibrations

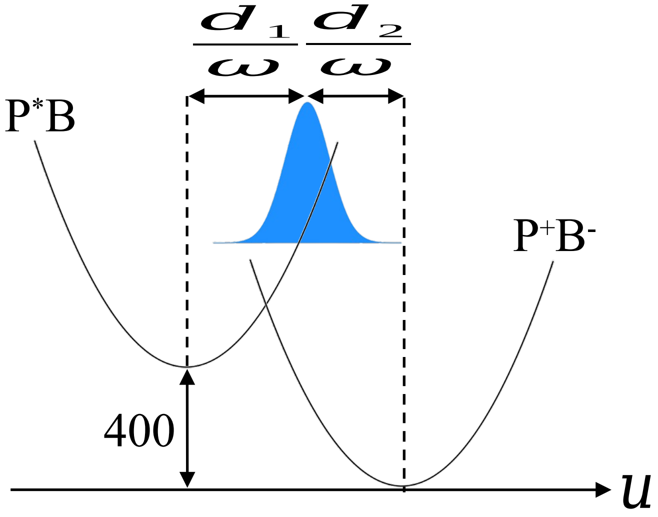


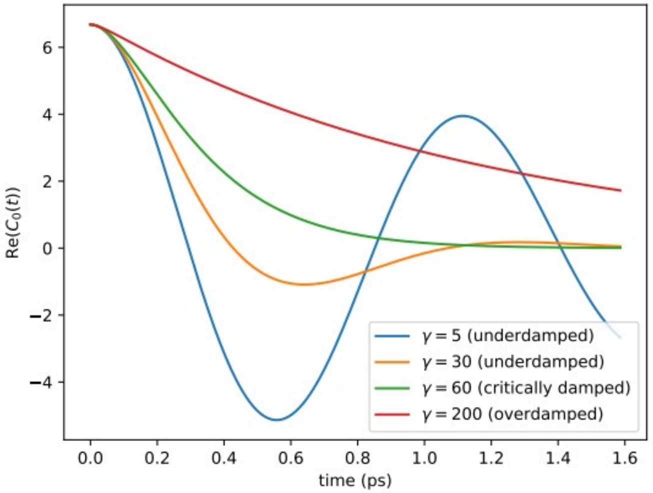
Fuller, *et al.* Nat. Chem., 6, 706-711, (2014)



Low-frequency, off-resonant, underdamped vibrational modes can assist electron transfer

Modeling the effect of an underdamped mode





Long vibrational coherence time
→ Memory effect
→ Non-Markovian equations of motion

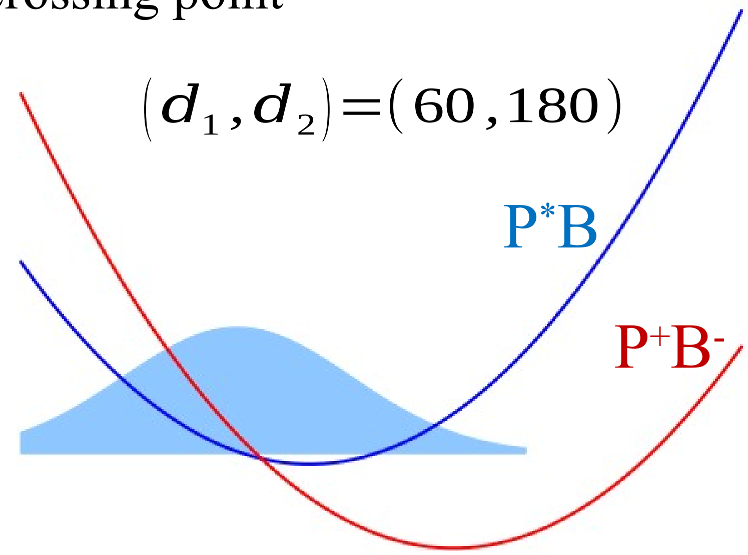
Hierarchical equations of motion (HEOM):

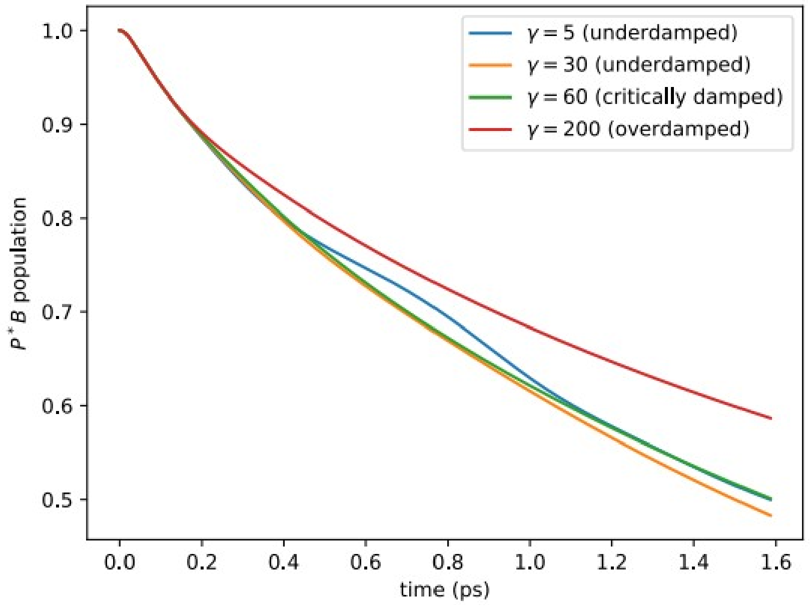
$$\frac{d}{dt}\rho^{n,m} = -iH^{\times}\rho^{n,m} - \frac{\gamma}{2}(n+m)\rho^{n,m} - S^{\times}\rho^{n+1,m}$$
$$+nc_0(0)S^{\times}\rho^{n-1,m} + m\left(Re\left(c_1(0)\right)S^{\times} + iIm\left(c_1(0)\right)S^{o}\right)\rho^{n,m-1}$$
$$+nk_{01}\rho^{n-1,m+1} + mk_{10}\rho^{n+1,m-1}$$

Damping effects

Set cm-1 (i.e., off-resonant, low-frequency) and vary . **Underdamped** modes assist the electron transfer the best. Damping effects depend strongly on the position of the initial nuclear position.

Configuration 1: initial nuclear position on the same side as the crossing point



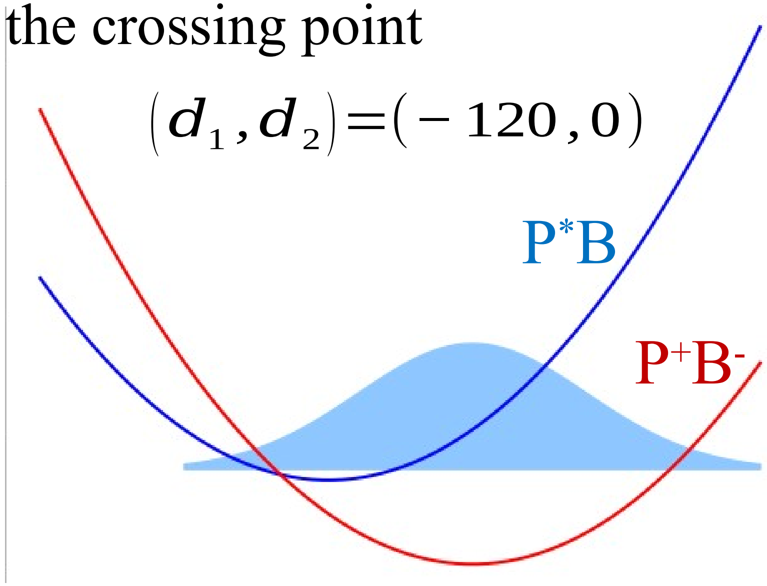


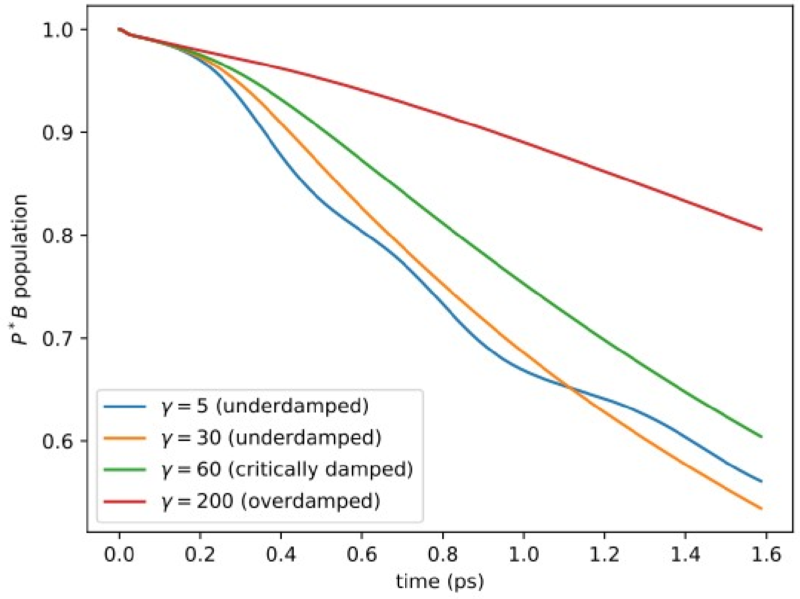
Damping effects

Set cm^{-1} (i.e., off-resonant, low-frequency) and vary . **Underdamped** modes assist the electron transfer the best. Damping effects depend strongly on the position of the initial nuclear position.

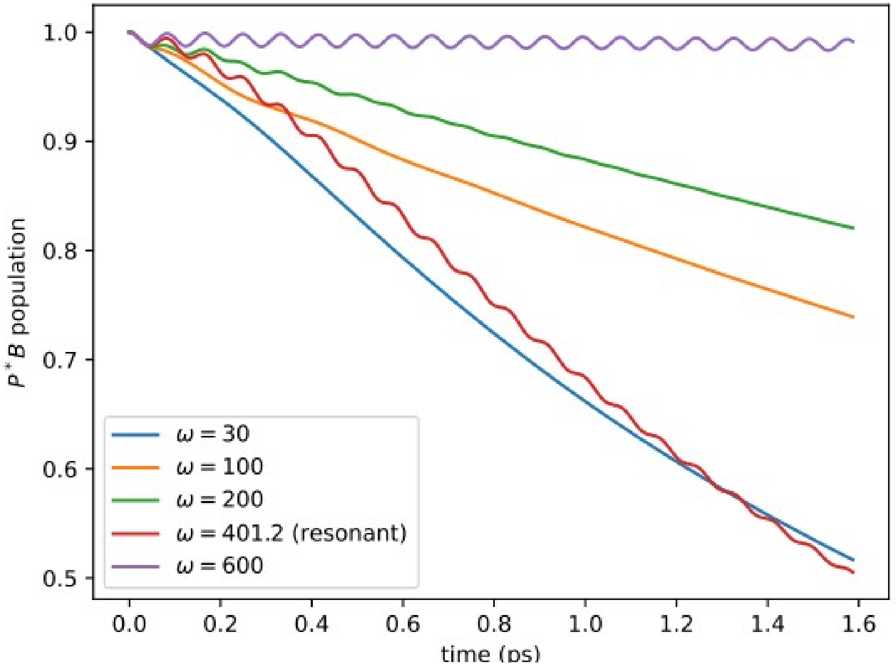
Configuration 2: initial nuclear position on the opposite side of the crossing point

$$(d_1, d_2) = (-120, 0)$$





Frequency effects



Set cm^{-1} and vary . Electron transfer is enhanced when the mode frequency is **resonant** or **off-resonant at low frequency**.

Low-frequency, off-resonant, underdamped vibrational modes can assist electron transfer

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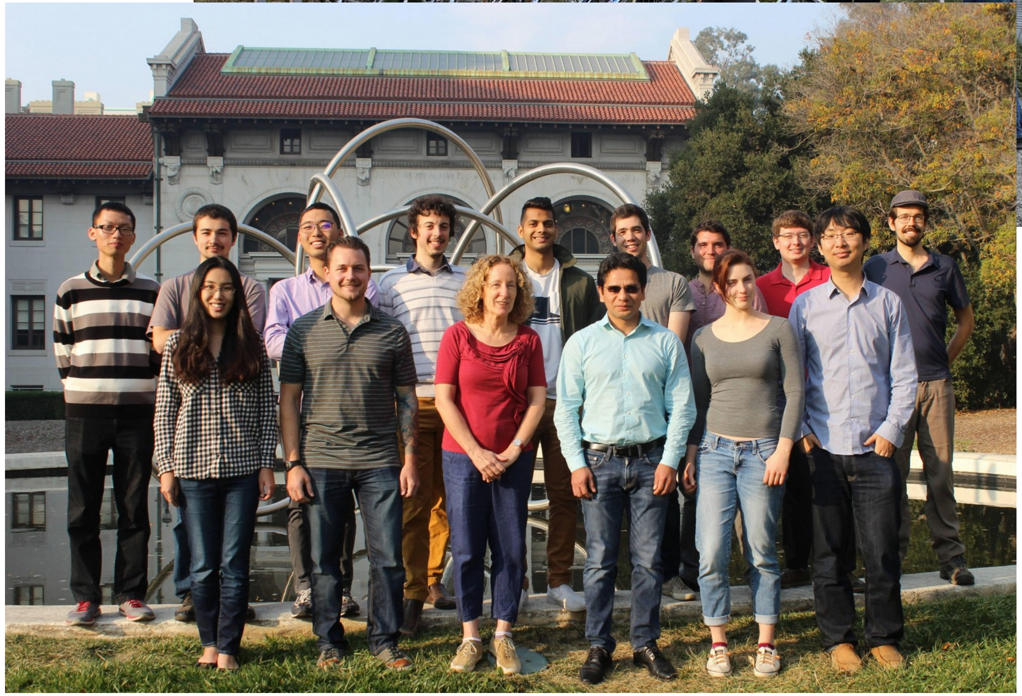


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12