Quantum Resonance Theory of Open System Dynamics

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The results presented are based on collaborations with

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Open quantum systems

System S coupled to reservoir R of harmonic oscillators

$$H = H_S + \underbrace{\sum_k \omega_k a_k^\dagger a_k}_{H_R} + \lambda\, G \otimes \Big(\sum_k g_k a_k^\dagger + \mathrm{h.c.} \Big)$$

$$H_S = \sum_{j=1}^{d} E_j |\phi_j\rangle\langle\phi_j|$$

λ = coupling constant ($\in \mathbb{R}$)

G = coupling matrix

g_k = form factor ($\in \mathbb{C}$)

Reduced system dynamics

Initial SR density matrix: $\rho_{SR}(0)$

Reduced density matrix of system:

$$\rho_S(t) = \mathrm{tr}_R\Big(\mathrm{e}^{-\mathrm{i}tH}\rho_{SR}(0)\,\mathrm{e}^{\mathrm{i}tH}\Big)$$

In case $\rho_{SR}(0) = \rho_S(0) \otimes \rho_R(0) \Rightarrow$ well defined **dynamical map**

$$V(t)\rho_S(0) = \rho_S(t)$$

- $V(t)$ is **not a group**: $V(t+s) \neq V(t)V(s)$
- $\forall t$, $V(t)$ is **completely positive, trace preserving (CPT)**
- **Markovian approximation**: $V(t) \approx \mathrm{e}^{t\mathcal{L}}$ CPT semigroup

Resonance theory

Goal

Find a manageable approximation for $\rho_S(t)$ that

– captures irreversible effects (*e.g.* decay rates)
– is valid for all times (no "$\lambda^2 t < \mathrm{const}$" constraint)
– has a controlled error (λ small, time arbitrary)

Basic philosophy

(1) Start with coupled SR Hamiltonian H

Irreversible dynamics $\leftrightarrow$ continuous mode limit of reservoir

(2) Do spectral analysis of H by perturbation theory (λ small)

Eigenvalues $\leftrightarrow$ stationary (bound) states
Resonances $\leftrightarrow$ metastable states
Continuous spectrum $\leftrightarrow$ "scattering states"

Thermodynamic limit

Consider (for instance) reservoir equilibrium state $\rho_{R,\beta} \propto e^{-\beta H_R}$ and perform thermodynamic limit

Limit state is represented by a vector in a purified (new) Hilbert space; has simple, explicit expression

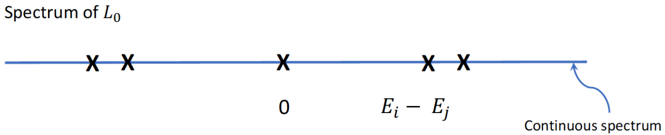
$$\rho_{R,\beta} \quad \rightsquigarrow \quad |\Omega\rangle$$

In the new space, Hamiltonian H takes different form, called *Liouvillian* L

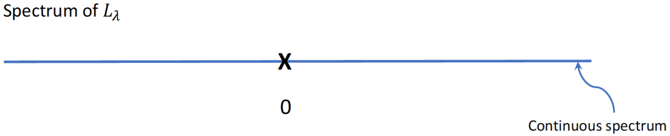
$$\mathrm{e}^{\mathrm{i}tH} \quad \rightsquigarrow \quad \mathrm{e}^{\mathrm{i}tL}$$

Spectral analysis of $L_\lambda = L_0 + \lambda I$

(A) $\lambda = 0$: L_0 has eigenvalues $E_i - E_j$ embedded in continuous spectrum, 0 is degenerate (multiple stationary states)



(B) $\lambda \neq 0$: Eigenvalues are generically unstable, degeneracy of 0 is lifted: unique stationary state (equilibrium)

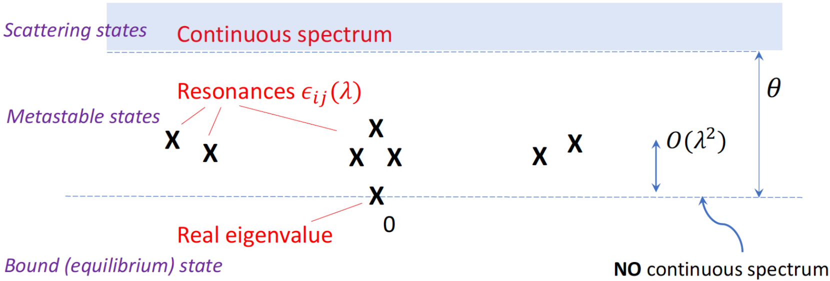


Unstable eigenvalues become complex resonances

– 'Deform' operator $L_\lambda \rightsquigarrow L_\lambda(\theta)$ by *complex scaling*:
  - θ moves continuous spectrum away from eigenvalues
  - uncovers new, complex eigenvalues
  - works if *reservoir correlation function decays in time*

– Analytic perturbation theory: $\epsilon_{ij}(\lambda) = E_i - E_j + \lambda^2 \epsilon'_{ij} + \cdots$

Spectrum of $L_\lambda(\theta)$ in $\mathbb{C}$



Expressing propagator via resonances

– When sandwiched between (suitable) states $\langle\Psi| \cdot |\Phi\rangle$, true propagator e^{itL} can be replaced by deformed propagator $e^{itL(\theta)}$

– Spectral decomposition:

$$e^{\mathrm{i}tL(\theta)} = \sum_j e^{it\epsilon_j(\lambda)} P_j(\lambda) + O(e^{-\theta t})$$

$$\epsilon_j(\lambda) = e + \lambda^2 \epsilon_j^{(2)} + O(\lambda^4)$$

$$e^{it\epsilon_j(\lambda)} = e^{it\mathrm{Re}\,\epsilon_j(\lambda)} e^{-t\mathrm{Im}\,\epsilon_j(\lambda)}$$

Decay rates: $\mathrm{Im}\epsilon_j(\lambda) \propto \lambda^2$ (or $O(\lambda^4)$...), decay directions: $P_j(\lambda)$

Result 1: Resonance expansion of dynamics

ρ_{SR} = initial SR state

$\rho_{S,\beta,\lambda}$ = full equilibrium state $\propto e^{-\beta H_\lambda}$ reduced to S

For all λ small, $t \geq 0$, system observable X:

$$\begin{aligned}
&\mathrm{tr}_{SR}\Big(\rho_{SR}\ e^{itH_\lambda} X e^{-itH_\lambda}\Big) \\
&\quad = \ \mathrm{tr}_S\big(\rho_{S,\beta,\lambda} X\big) + \sum_j e^{it\epsilon_j(\lambda)}\ \mathrm{tr}_{SR}\Big(\rho_{SR}\big(P_j X \otimes \mathbf{1}_R\big)\Big) \\
&\qquad + O\Big(\lambda e^{-\gamma(\lambda)t}\Big)
\end{aligned}$$

Here, $\gamma(\lambda) = \min_j\{\mathrm{Im}\epsilon_j(\lambda)\}$ and P_j are λ-independent projections

Result 2: Markovian approx is valid <u>for all</u> times

$\rho_{SR} = \rho_S \otimes \rho_{R,\beta} \Rightarrow$ dynamical map $V(t)\rho_S = \rho_S(t)$ well defined

Suppose *"Fermi Golden Rule holds"*:

$$\gamma_{\mathrm{FGR}} \equiv \min_j \mathrm{Im}\epsilon_j^{(2)} > 0$$

where $\epsilon_j^{(2)}$ is the second order term of $\epsilon_j(\lambda)$ in λ. Then

$$\left\| V(t) - e^{t(\mathcal{L}_S + \lambda^2 K)} \right\| \leq C\lambda^2, \qquad \text{for all } t \geq 0$$

$\mathcal{L}_S = -\mathrm{i}[H_S, \,\cdot\,]$, K is the "Davies generator"

This result overcomes "$\lambda^2 t < \mathrm{const.}$" regime

Previously, only *weak coupling- or, Van Hove regime* was treated rigorously:

[Davies '73, '74] $\forall a > 0$

$$\lim_{\lambda \to 0} \sup_{0 \le \lambda^2 t < a} \left\| V(t) - \mathrm{e}^{t(\mathcal{L}_0 + \lambda^2 K)} \right\| = 0$$

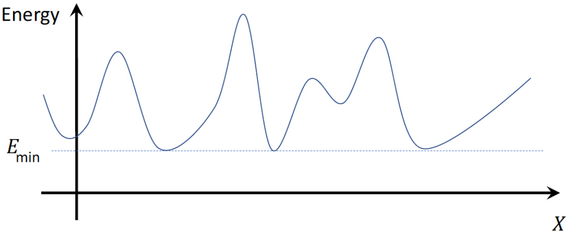
Resonance theory eliminates constraint $\lambda^2 t < \mathrm{const.}$!

Illustration: Electron transport in degenerate donor-acceptor systems

Collaboration with A. Saxena and G.P. Berman, in progress

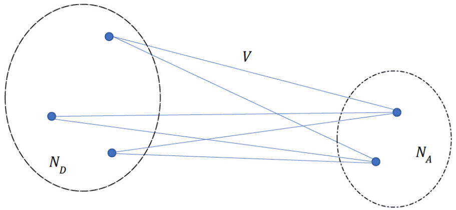
N_D, N_A fold degenerate donor, acceptor in thermal enviornment:

$$H = H_S + \sum_k \omega_k a_k^\dagger a_k + \lambda G \otimes \sum_k \left(g_k a_k^\dagger + \mathrm{h.c.} \right)$$



Energy landscape for Donor/Acceptor: degenerate minima

Homogeneous coupling between donor and acceptor levels



$$H_S = E_D \sum_{j=1}^{N_D} |D_j\rangle\langle D_j| + E_A \sum_{k=1}^{N_A} |A_k\rangle\langle A_k| + V \sum_{j,k} \left(|A_k\rangle\langle D_j| + |D_j\rangle\langle A_k|\right)$$

Diagonal coupling to noise

$$G = g_D \sum_{j=1}^{N_D} |D_j\rangle\langle D_j| + g_A \sum_{k=1}^{N_A} |A_k\rangle\langle A_k|$$

Symmetry of Hamiltonian $\Rightarrow$ invariant subspaces

$$H = H_{\mathrm{eff}} \oplus H_{D\perp} \oplus H_{A\perp}$$

- H_{eff} is an effective open 2-level system on $\mathrm{span}\{|D\rangle, |A\rangle\}$

$$|D\rangle = \tfrac{1}{\sqrt{N_D}} \sum_{j=1}^{N_D} |D_j\rangle, \qquad |A\rangle = \tfrac{1}{\sqrt{N_A}} \sum_{k=1}^{N_A} |A_k\rangle$$

- $H_{D\perp}, H_{A\perp}$ act on states orthogonal to $|D\rangle$ and $|A\rangle$ (& on R)
- Via *polaron transformation*, $H_{D\perp}$, $H_{A\perp} = H_R + \mathrm{const.}$

$\Rightarrow$ multitude of stationary states $\rho_S \otimes \rho_{R,\beta}^{\mathrm{dressed}}$

Resonance theory: dynamics of DA density matrix for general initial state ρ_0

$$\rho_t = \mathrm{Tr}(\rho_0 P_S^{\mathrm{eff}})\ \rho_{S,\beta}^{\mathrm{eff}} + P_{D\perp}\rho_0 P_{D\perp} + P_{A\perp}\rho_0 P_{A\perp}$$

$$+2\mathrm{Re}\ e^{it\epsilon_4^{(3)}} P_{A\perp}\rho_0 P_{D\perp}$$

$$+\frac{e^{it\epsilon_1^{(2)}}}{e^{-\beta e_1}+e^{-\beta e_2}}\Big[e^{-\beta e_2}P_{11}\rho_0 P_{11} - e^{-\beta e_2}P_{21}\rho_0 P_{12}$$

$$-e^{-\beta e_1}P_{12}\rho_0 P_{21} + e^{-\beta e_1}P_{22}\rho_0 P_{22}\Big]$$

$$+2\mathrm{Re}\ e^{it\epsilon_1^{(3)}} P_{22}\rho_0 P_{11} + 2\mathrm{Re}\ \sum_{s=1,2} e^{it\epsilon_2^{(s)}} P_{D\perp}\rho_0 P_{ss}$$

$$+2\mathrm{Re}\ \sum_{s=3,4} e^{it\epsilon_2^{(s)}} P_{A\perp}\rho_0 P_{(s-2)(s-2)} + O(\lambda^2)$$

– Diabatic DA energies $e_{1,2}$, states $\{\varphi_1, \varphi_2\}$, $P_{ij} = |\varphi_i\rangle\langle\varphi_j|$
– Error is independent of t and N_D, N_A

Total donor population at time t

$$p_D(t) \equiv \sum_{k=1}^{N_D} \langle D_k, \rho_t D_k \rangle$$

- Resonance theory gives (modulo $O(\lambda^2)$)

$$\begin{aligned} p_D(t) &= p_D(0) - (1 - e^{it\epsilon_1^{(2)}}) \frac{1-\alpha^2}{1+\alpha^2} \; \frac{e^{-\beta e_2}[\rho_0]_{11} - e^{-\beta e_1}[\rho_0]_{22}}{e^{-\beta e_1} + e^{-\beta e_2}} \\ & -2\frac{|\alpha|}{1+\alpha^2} \,\mathrm{Re}(1 - e^{it\epsilon_1^{(3)}})[\rho_0]_{21} \\ & -2\mathrm{Re} \sum_{k=1}^{N_D} \sum_{s=1,2} (1 - e^{it\epsilon_2^{(s)}}) \langle D_k, P_{D\perp} \rho_0 P_{ss} D_k \rangle \end{aligned}$$

- Note: several decay rates (all explicit)

Coherent/incoherent spread of initial donor population

$p_1, \ldots, p_{N_D}$: a probability distribution, $0 \leq p_j \leq 1$, $\sum_j p_j = 1$

Consider two families of initial states:

(inc) The incoherent (classical) superposition

$$\rho_{\mathrm{inc}} = \sum_{j=1}^{N_D} p_j |D_j\rangle\langle D_j|$$

(coh) The coherent (quantum) superposition pure state

$$\rho_{\mathrm{coh}} = |\psi\rangle\langle\psi| \quad \text{where} \quad |\psi\rangle = \sum_{j=1}^{N_D} \sqrt{p_j}|D_j\rangle$$

Final donor population: classical initial state

Independent of distribution $\{p_j\}$

$$p_{D,\mathrm{inc}}(\infty) \approx \begin{cases} 1 - \dfrac{1}{2N_D}, & T \gg e_1 - e_2 \\[2ex] 1 - \dfrac{1}{N_D(1+\alpha^2)}, & T \ll e_1 - e_2. \end{cases}$$

Acceptor not populated for large N_D

Final donor population: quantum initial state

Depends on $\{p_j\}$

$$p_{D,\mathrm{coh}}(\infty) \approx \begin{cases} 1 - \left(\sum_{k=1}^{N_D} \sqrt{p_k} \right)^2 \frac{1}{2N_D}, & T \gg e_1 - e_2 \\ 1 - \left(\sum_{k=1}^{N_D} \sqrt{p_k} \right)^2 \frac{1}{N_D(1+\alpha^2)}, & T \ll e_1 - e_2. \end{cases}$$

- Low temp & $p_k = 1/N_D \quad \Rightarrow \quad p_{D,\mathrm{coh}}(\infty) = 1 - \frac{1}{1+\alpha^2}$
- **Depletion of donor = total population of acceptor** $(\alpha = 0)$

$$p_{D,\mathrm{coh}}(\infty) \approx 0 \qquad \text{if} \quad T \text{ and } V\sqrt{N_D N_A} \ll E_D - E_A$$

Upshot

- Coherent (quantum) spread of initial excitation on donor sites enhances transfer efficiency
- Acceptor population maximized for coherent, uniformly spread initial excitation, can get fully populated at low temperature
- For large N_D and incoherent (classical) initial spread, transfer efficiency is always low

Conclusion

Resonance theory

- gives expansion of system dynamics for small λ, all t
- gives decay rates, decay directions
- shows Markovian approximation is valid for all times
- furnishes explicit expressions suitable for detailed analysis