



## The Spin-Boson Model, Part II.

### Topics covered:

- 1) Improved (non-Markovian) Kinetic Master Equations for the system state populations: a partial derivation.
- 2) Specialization of these non-Markovian Master Equations to the Spin-Boson model: the Non-Interacting Blip Approximation (NIBA).
- 3) NIBA predictions for the Spin-Boson dynamics: some case studies.
- 4) The strong electron-phonon coupling regime according to NIBA (Golden Rule): Marcus Theory rate constants.
- 5) Supplemental notes on the (sinusoidally) Driven Spin-Boson Problem:
  - i) Golden-rule analysis of the short-time dynamics: altered rate constants (!)
  - ii) the field-driven NIBA equations.

①

A better observation of the Kinetic Master Eqs.:

Consider the Quantum Liouville Eq:  $\frac{\partial \rho}{\partial t} = -i [H, \rho]$

If  $H = H_0 + V$ , and then defining  $\rho_{\pm}(t) = e^{-iH_0 t} \rho(t) e^{iH_0 t}$ ; and  $H_{\pm}(t) = e^{iH_0 t} V e^{-iH_0 t}$

then:

$$\frac{\partial \rho_{\pm}}{\partial t} = -i [H_{\pm}(t), \rho_{\pm}(t)] \quad [1]$$

N.B.: Here  $\hat{\rho}_{\pm}(t)$ ,  $\hat{\rho}_{\pm}(t)$  refer to the subsystem density operator.

A formal solution is:

$$\rho_{\pm}(t) = \rho_0 - i \int_0^t dt' [H_{\pm}(t'), \rho_{\pm}(t')] \quad [2]$$

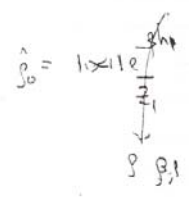
Substitute [2] into [1]:

$$\frac{\partial \rho_{\pm}}{\partial t} = -i [H_{\pm}(t), \rho_0] = \int_0^t dt' [H_{\pm}(t), [H_{\pm}(t'), \rho_{\pm}(t')]] \quad [3] \text{ (exact)}$$

Now specialize to a two-electronic state nonadiabatic transitions problem:

$$H_0 = |1\rangle\langle 1| h_1 + |2\rangle\langle 2| h_2; \quad V = (|1\rangle\langle 2| + |2\rangle\langle 1|) \Delta$$

$$H_{\pm}(t) = \begin{pmatrix} |1\rangle\langle 1| e^{i h_1 t} & -i \Delta e^{-i h_1 t} \\ -i \Delta e^{i h_2 t} & |2\rangle\langle 2| e^{i h_2 t} \end{pmatrix} \Delta$$



Apply  $\langle \alpha | \dots | \alpha \rangle \Rightarrow \frac{d}{dt} \langle \alpha | \rho_{\pm}(t) | \alpha \rangle = - \int_0^t dt' \langle \alpha | [H_{\pm}(t), [H_{\pm}(t'), \rho_{\pm}(t')]] | \alpha \rangle dt'$ ;  $\alpha = 1, 2$

N.B.:  $\langle \alpha | H_{\pm}(t) \rho_0 | \alpha \rangle = \langle \alpha | \rho_0 H_{\pm}(t) | \alpha \rangle = 0$

②

Now examine:

$$\begin{aligned}
 \langle 11 | [H_I(t), [H_2(t), \rho_I(t')]] | 11 \rangle &= H_I(t) \{ H_2(t) \rho_I(t') - \rho_I(t') H_2(t) \} - \{ H_2(t) \rho_I(t') - \rho_I(t') H_2(t) \} H_I(t) \\
 &\downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \\
 &= \int e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \langle 1 | \rho_I(t') | 1 \rangle - e^{i h_1 t} e^{-i h_2 t} \langle 4 | \rho_I(t') | 2 \rangle e^{i h_2 t'} e^{-i h_1 t'} \\
 &\quad - e^{-i h_1 t} e^{-i h_2 t'} \langle 2 | \rho_I(t') | 2 \rangle e^{i h_2 t} e^{-i h_1 t} + \langle 1 | \rho_I(t') | 1 \rangle e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \delta^2
 \end{aligned}$$

Further

$$\begin{aligned}
 \frac{1}{\delta^2} \text{tr}_x \langle 11 | [I, [I, t]] | 11 \rangle &= \text{tr}_x \int_0^t \int_0^t e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \langle 1 | \rho_I(t') | 1 \rangle \\
 &\quad - 2 \text{Re} \text{tr}_x \int_0^t \int_0^t e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \langle 2 | \rho_I(t') | 2 \rangle
 \end{aligned}$$

Thus, we have exact (generalized) Master Eq.:

$$\begin{aligned}
 (i) \frac{1}{\delta^2} \frac{d}{dt} \text{tr}_x \langle 1 | \rho_I(t) | 1 \rangle &= - \int_0^t dt' \left[ 2 \text{Re} \text{tr}_x \int_0^t e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \langle 1 | \rho_I(t') | 1 \rangle \right. \\
 &\quad \left. - 2 \text{Re} \text{tr}_x \int_0^t e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \langle 2 | \rho_I(t') | 2 \rangle \right]
 \end{aligned}$$

That is:  $\hat{\rho}_I(t) = \hat{\rho}_{\beta,1} \cdot \hat{\rho}_I^s(t)$  ← 2x2 system density matrix  
 ↑ thermal density operator for surface 1 harmonic oscillator.

(ii) analogously w/ 1 ↔ 2

Propose is made by assuming

$$\langle 1 | \rho_I(t) \rangle \approx \rho_{\beta,1}(t); \quad \langle 2 | \rho_I(t) \rangle = \rho_{\beta,2}(t)$$

in small Δ limit

$$\text{tr}_x \int_0^t e^{i h_1 t} e^{-i h_2(t-t')} e^{-i h_1 t'} \rho_{\beta,1} \} = \text{tr}_x \int_0^t e^{-i h_2(t-t')} e^{i h_1(t-t')} \rho_{\beta,1} \}$$

finally...

③

$$(\ddagger) \quad \frac{d p_1(t)}{dt} = - \int_0^t dt' \left\{ \underset{2 \leftarrow 1}{\cancel{\kappa}}(t-t') p_1(t') - \underset{1 \leftarrow 2}{\cancel{\kappa}}(t-t') p_2(t') \right\}$$

$$\frac{d p_2(t)}{dt} = - \int_0^t dt' \left\{ \underset{1 \leftarrow 2}{\cancel{\kappa}}(t-t') p_2(t') - \underset{2 \leftarrow 1}{\cancel{\kappa}}(t-t') p_1(t') \right\}$$

$$\omega \quad \underset{2 \leftarrow 1}{\kappa}(t) = \Delta^2 \text{Re tr}_X \left\{ e^{-i h_2 t} \underset{\beta, 1}{: h_1 t} \right\} \quad (\ddagger)$$

NB: Using projection operator techniques  $\times \times$ , it can be shown that exact generalized Master Eqs. of the form  $(\ddagger)$  exist with GME's

$$\underset{2 \leftarrow 1}{\kappa}(t) = \Delta^2 \underset{2 \leftarrow 1}{\kappa}^{(2)}(t) + \Delta^4 \underset{2 \leftarrow 1}{\kappa}^{(4)}(t) + \dots$$

the  $\kappa$ 's are independent of  $\Delta$

with

$$\underset{2 \leftarrow 1}{\kappa}^{(2)}(t) = 2 \text{Re tr}_X \left\{ e^{-i h_2 t} \underset{\beta, 1}{: h_1 t} \right\}$$

[exactly!]  $\left[ \begin{array}{l} \Delta^2 \underset{2 \leftarrow 1}{\kappa}^{(2)}(t) \\ \text{same as } (\ddagger) \end{array} \right]$

Thus, as  $\Delta \rightarrow 0$ , the GME's in  $(\ddagger)$  become exact (!)  $\leftarrow$  [one heeboo!]

Practical Question: how small a value of  $\Delta$  is "small enough" that  $\mathcal{O}(\Delta^4)$ , etc. can be neglected?

obviously, this depends on details of  $h_1, h_2$ , but there are many physically relevant situations (e.g. "Nonadiabatic" regime of polar electron transfer) where  $\mathcal{O}(\Delta^2)$  term suffices!

$\times \times$  M. Spontagnolo + S. Mukamel, J. Chem. Phys. 88, 3263 (88);  
Y. Hu + S. Mukamel, J. Chem. Phys. 91, 6973 (89).

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More on the NIBA: Same Case Studies

Recall the SB Hamiltonian in canonical form (following Leggett et al.):  $[k, m_j = 1]$

$$\hat{H} = \frac{1}{2} \Delta \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \frac{1}{2} \epsilon \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \frac{1}{2} \sum_k \left( \frac{p_k^2}{m} + \frac{1}{2} \omega_k^2 x_k^2 \right) + \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \sum_k g_k x_k$$

Also note:  $P_1(t) + P_2(t) = 1$ ; thus, there is only independent variable,  $\Theta(t) = P_1(t) - P_2(t)$

The NIBA equation of motion for  $\Theta(t)$  is:

$$\dot{\Theta}(t) = \int_0^t h(t-t') - \int_0^t dt' g(t-t') \Theta(t')$$

with:

$$g(t) = \Delta^2 \cos(\epsilon t) \cos\left(\frac{1}{\hbar} \Phi_1(t)\right) \exp\left\{-\frac{1}{\hbar} \Phi_2(t)\right\}$$

$$h(t) = \Delta^2 \sin(\epsilon t) \sin\left(\frac{1}{\hbar} \Phi_1(t)\right) \exp\left\{-\frac{1}{\hbar} \Phi_2(t)\right\}$$

and:

$$\Phi_1(t) = \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \sin(\omega t)$$

$$\Phi_2(t) = \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [1 - \cos(\omega t)] \coth\left(\frac{\omega}{2kT}\right)$$

where:  $J(\omega) = \frac{\pi}{2} \sum_j \frac{C_j^2}{\omega_j} \delta(\omega - \omega_j)$  ← Spectral density  
[characterizes oscillator bath and its coupling to the 2-level system]

For simplicity, specialize to symmetric SB model ( $\epsilon = 0$ ); also  $P_1(0) = 1 \Rightarrow \Theta(0) = 1$

$$\dot{\Theta} = - \int_0^t g(t-t') \Theta(t') dt' \Rightarrow s\hat{\Theta}(s) - 1 = -g(s)\hat{\Theta}(s) \Rightarrow \hat{\Theta}(s) = \frac{1}{s + g(s)}$$

$$\hat{\Theta}(s) \equiv \int_0^\infty e^{-st} \Theta(t) dt$$

Invert this Laplace transform to determine  $\Theta(t)$ .

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Again, for completeness, analyze the case of Ohmic Spectral Density

Ohmic bath:  $J(\omega) = \eta \omega e^{-\omega/\omega_c}$ ;  $\alpha \equiv \eta/\omega_c$

consider  $T=0$ ;  $\phi_1(t) = \eta \tan^{-1}(\omega_c t)$ ;  $\phi_2(t) = \frac{\eta}{2} \ln(1 + (\omega_c t)^2)$

Or:  $g(t) = \frac{\Delta^2}{\omega_c} \frac{\cos[2\alpha \tan^{-1}(\omega_c t)]}{[1 + (\omega_c t)^2]^\alpha}$ ;  $T=0$  Ohmic

Note  $g(t) \rightarrow 0$  as  $t \rightarrow \infty$

So try local kinetics approx,  $\dot{\phi} = -k\phi$ , w  $k = \int_0^\infty dt g(t) = \begin{cases} \infty, & \alpha < \frac{1}{2} \\ \frac{\Delta^2}{\omega_c} \cdot \frac{\pi}{2}, & \alpha = \frac{1}{2} \\ 0, & \alpha > \frac{1}{2} \end{cases}$

Only for  $\alpha = \frac{1}{2}$  [Toulouse limit] is expo. decay predicted, namely

$\phi(t) \approx e^{-kt}$ ;  $k = \frac{\pi}{2} \frac{\Delta^2}{\omega_c}$  Leggett. Eq. (5.23)

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$[T=0]$

Otherwise, analysis shows, for:  $0 < \alpha < \frac{1}{2}$ , damped oscillations  $[0 \rightarrow 0$  as  $t \rightarrow \infty]$  (high confidence)

$1 > \alpha > \frac{1}{2}$ , incoherent relaxation  $[O(t) > 0$  always  $\rightarrow 0$  as  $t \rightarrow \infty]$  ("currently unresolved problem")

$\alpha > 1$  Localization (confidence)

At finite Temps :

$0 < \alpha < 1$ ,  $\alpha T \geq \Delta_V$  Exponential relaxation w rate  $\propto T^{2\alpha-1}$

See Logg

except (?) at

$\alpha = \frac{1}{2}$ ; expo relaxation w rate  $\pi \Delta^2 / 2\omega_c$  [same as  $T=0$ ]

$\alpha > 1$ , expo. relaxation w rate  $\propto T^{2\alpha-1}$

Subohmic case, i.e.  $0 < S < 1$ :

$T=0$ ; Localization

See Logg

$-(T_0/\pi)^{1-S}$

$T > 0$ ; Expo. relaxation w rate  $\propto e$

Superohmic case:

$1 < S < 2$  damped oscillations at  $T=0$ ;

exponential relaxation for  $T > T_0^*$

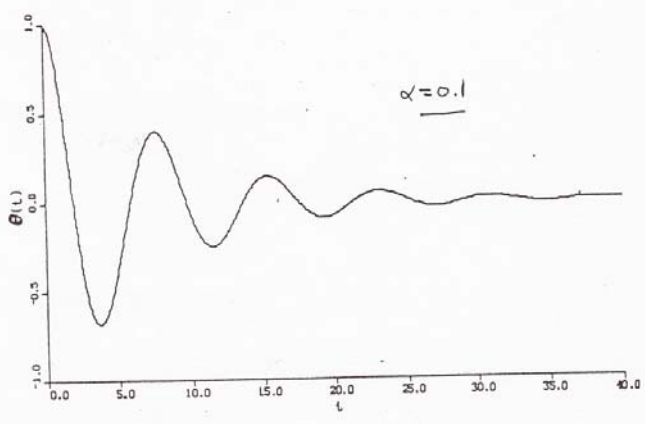
See Logg

adiabatically narrowed but tunneling constant

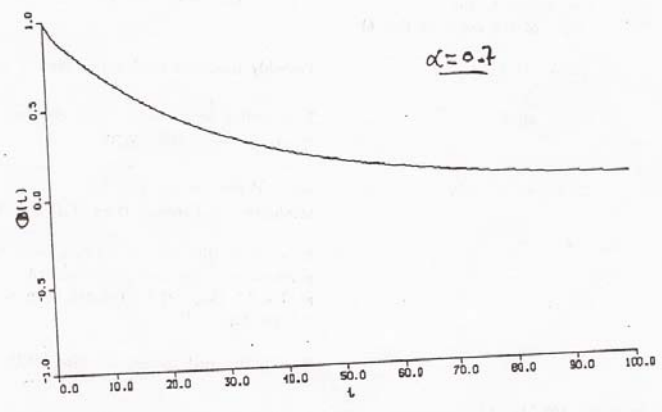
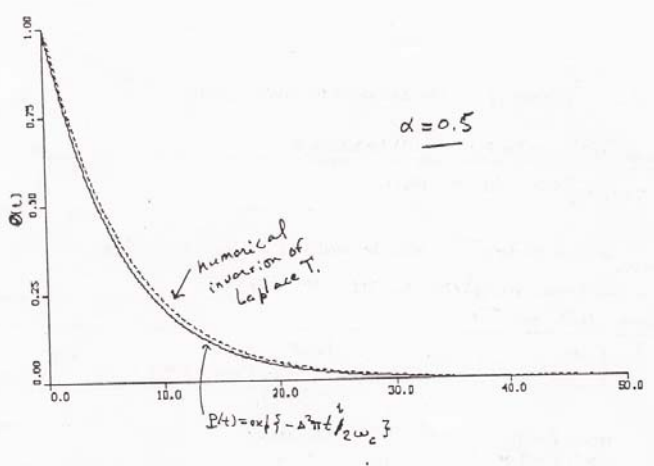
$S > 2$  Exponentially damped sinusoidal oscillation  $O(t) = \cos \tilde{\Delta} t e^{-\kappa t}$

$\kappa \sim \kappa_{\text{golden rule}}$

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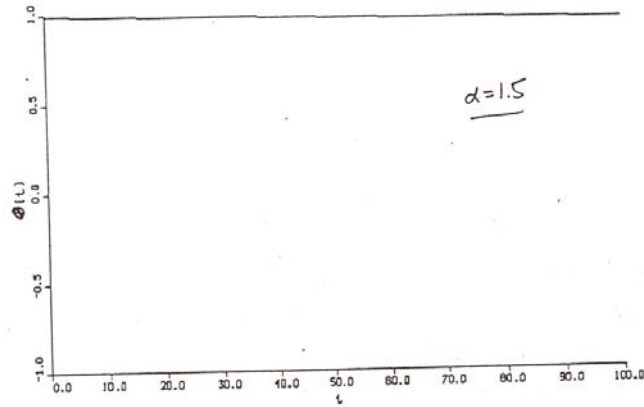


Chmic Spectral  
Density  
 $\omega/\omega_c$   
 $J(\omega) = \gamma \omega e$   
 $[\alpha = \gamma/2\pi]$



} nonexponential  
(algebraic)  
decay  
 $\sim \frac{1}{t^{2(1-\alpha)}}$





Leggett *et al.*: The dissipative two-state system

TABLE I. Summary of results for  $P(t) \equiv \langle \sigma_x(t) \rangle$  for bias  $\epsilon = 0$ .

$$H = -\frac{1}{2}\hbar\Delta\sigma_x + \frac{1}{2}q_0\sigma_z + \sum_a C_a x_a + H_b(\{m_a\}, \{\omega_a\}),$$

$$J(\omega) \equiv \frac{\pi}{2} \sum_a \frac{C_a^2}{m_a \omega_a} \delta(\omega - \omega_a) = A \omega^\alpha e^{-\omega/\omega_c} \quad \text{with the conditions } \Delta \ll \omega_c, \quad k_B T \ll \hbar\omega_c.$$

Other quantities used below:  $\alpha \equiv \eta q_0^2 / 2\pi\hbar$ ,  $\Delta_r = \Delta(\Delta/\omega_c)^{\alpha/(1-\alpha)}$  ( $\alpha < 1$ ).

Ohmic dissipation:  $J(\omega) = \eta \omega e^{-\omega/\omega_c}$ .

$0 < s < 1$	$T = 0$ $T \neq 0$	Localization exponential relaxation with a rate $\propto \exp[-(T_0/T)^{1-\alpha}]$ (Sec. VI.A)
$s = 1$ (ohmic)	$\alpha > 1, T = 0$ $\alpha > 1, T \neq 0$ or $\alpha < 1, \alpha T \geq \Delta_r$ (i.e., region to the right of the curve in Fig. 8)	Localization  Exponential relaxation with a rate $\propto T^{2\alpha-1}$ (Sec. V.C)
	$\frac{1}{2} < \alpha < 1, T \lesssim \Delta_r$	Probably incoherent relaxation (Sec. V.E)
	$\alpha = \frac{1}{2}, \text{ all } T$	Exponential decay with a rate $\pi\Delta^2/2\omega_c$ (Toulouse limit) (Sec. V.B)
	$0 < \alpha < \frac{1}{2}, \alpha T \lesssim \Delta_r$	Damped oscillations with an incoherent background (Secs. V.D and V.F)
$1 < s < 2$		Damped oscillations at $T=0$ , with a crossover to exponential relaxation at $T=T^*$ (Sec. VI.B); for definition of $T^*$ see Eq. (6.42)
$s > 2$		Weakly damped oscillations (Sec. VI.B)

For results for  $\epsilon \neq 0$ , see Sec. VII.

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Short-time, High-Temperature Gaussian Approximation to Golden-Rule (NIBA)  
Time kernels and Rate Constants - "Marcus Theory"

Write the NIBA (non-Markovian) Master Equations in  $\dot{P}_1, \dot{P}_2$  form:

$$\dot{P}_1(t) = -\int_0^t dt' \kappa_{2 \leftarrow 1}(t-t') P_1(t') + \int_0^t dt' \kappa_{1 \leftarrow 2}(t-t') P_2(t')$$

$$\dot{P}_2(t) = \int_0^t dt' \kappa_{1 \leftarrow 2}(t-t') P_1(t') - \int_0^t dt' \kappa_{2 \leftarrow 1}(t-t') P_2(t')$$

with:

$$\kappa_{2 \leftarrow 1}(t) = \frac{\Delta^2}{2} e^{-\frac{\Phi_2(t)}{\hbar}} \cos\left[\frac{\Phi_1(t)}{\hbar} + \epsilon t\right]$$

$$\kappa_{1 \leftarrow 2}(t) = \frac{\Delta^2}{2} e^{-\frac{\Phi_2(t)}{\hbar}} \cos\left[\frac{\Phi_1(t)}{\hbar} - \epsilon t\right]$$

[Note connection to "0" form:  $0 = P_1 - P_2$ ;  $1 = P_1 + P_2 \Rightarrow \kappa_{2 \leftarrow 1} = \frac{g-h}{2}$ ;  
 $\kappa_{1 \leftarrow 2} = \frac{g+h}{2}$  ]

In Markovian

(rate constant) regime:

$$\dot{P}_1 = -k_{2 \leftarrow 1} P_1 + k_{1 \leftarrow 2} P_2$$

$$\dot{P}_2 = k_{2 \leftarrow 1} P_1 - k_{1 \leftarrow 2} P_2$$

with:

$$k_{2 \leftarrow 1} = \frac{\Delta^2}{2} \int_0^\infty dt e^{-\frac{\Phi_2(t)}{\hbar}} \cos\left(\frac{\Phi_1(t)}{\hbar} + \epsilon t\right) = \frac{\Delta^2}{4} \int_{-\infty}^\infty dt e^{-\frac{\Phi_2(t)}{\hbar}} e^{i\left(\frac{\Phi_1(t)}{\hbar} + \epsilon t\right)}$$

$$k_{1 \leftarrow 2} = \frac{\Delta^2}{2} \int_0^\infty dt e^{-\frac{\Phi_2(t)}{\hbar}} \cos\left(\frac{\Phi_1(t)}{\hbar} - \epsilon t\right) = \frac{\Delta^2}{4} \int_{-\infty}^\infty dt e^{-\frac{\Phi_2(t)}{\hbar}} e^{i\left(\frac{\Phi_1(t)}{\hbar} - \epsilon t\right)}$$

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Now make the "short-time" approximation:

← Validity requires  $\omega t \ll 1$   
 $\omega t$  decay

$$\frac{\Phi_1(t)}{\pi} = \frac{1}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega^2} \sin(\omega t) \approx t \cdot \underbrace{\frac{1}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega}}_{E_r}$$

$\underbrace{\sin(\omega t)}_{[\omega t + \dots]}$

$$\frac{\Phi_2(t)}{\pi} = \frac{1}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega^2} [1 - \cos(\omega t)] \coth\left(\frac{\omega}{2kT}\right) = t^2 \cdot \frac{1}{2\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega} \coth\left(\frac{\omega}{2kT}\right)$$

$\underbrace{[1 - \cos(\omega t)]}_{\omega^2 t^2 / 2 + \dots}$

Further "progress" w/  $\Phi_2(t)$  is obtained by making high temperature approximation:  $\frac{\omega}{kT} \ll 1$

Then:  $\frac{\Phi_2(t)}{\pi} \approx t^2 \cdot \frac{1}{2\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega} \left[ \frac{2kT}{\omega} \right] = t^2 \cdot kT \cdot \underbrace{\frac{1}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega}}_{E_r}$

Note: validity requires  $\frac{\omega}{kT} \ll 1$

Now:

$$k_{z \leftarrow 1} = \frac{\Delta^2}{4} \int_{-\infty}^{\infty} dt e^{-E_r kT t^2 + i(E_r + \epsilon)t} = \frac{\Delta^2}{4} \left[ \frac{\pi}{E_r kT} \right]^{\frac{1}{2}} \exp\left\{ -\frac{(E_r + \epsilon)^2}{4 E_r kT} \right\}$$

Similarly:

$$k_{1 \leftarrow 2} = \frac{\Delta^2}{4} \left[ \frac{\pi}{E_r kT} \right]^{\frac{1}{2}} \exp\left\{ -\frac{(E_r - \epsilon)^2}{4 E_r kT} \right\}$$

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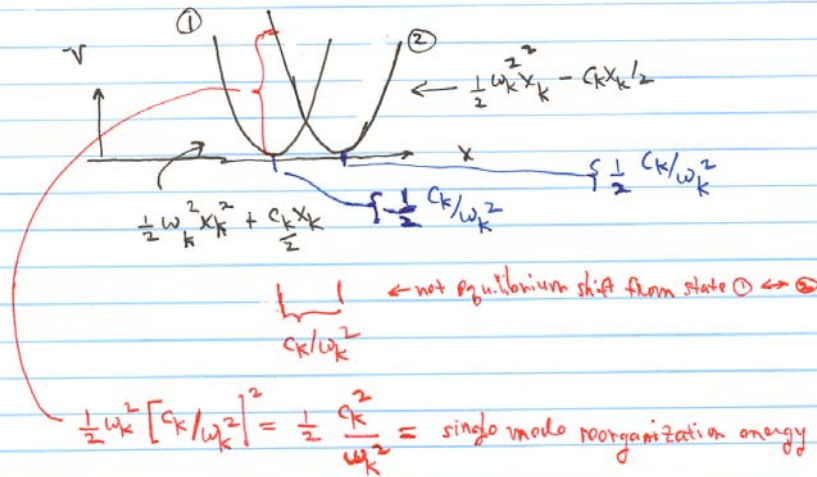
Final details of Marcus Theory:

1) What is  $E_r$ ?

$$E_r = \frac{1}{\pi} \int_0^{\infty} d\omega \frac{1}{\omega} \cdot \frac{\pi}{2} \sum_j c_j^2 \delta(\omega - \omega_j) = \frac{1}{2} \sum_j \frac{c_j^2}{\omega_j^2}$$

← (multi-mode) reorganization energy

Look at displacements in one phonon coordinate:



2) Consistency check: for polar electron transfer  $E_r \approx 1 \text{ eV}$ ;

$$\omega_c \sim 500 \text{ cm}^{-1}; \quad kT \approx 200 \text{ cm}^{-1}$$

$$i) (\omega_c \tau_{\text{decay}})^2 \approx \frac{\omega_c^2}{E_r kT} \approx \frac{(500 \text{ cm}^{-1})^2}{(8000 \text{ cm}^{-1})(200 \text{ cm}^{-1})} = \frac{25 \times 10^{-1}}{16} \ll 1$$

ii)  $\frac{kT}{\omega_c} = \frac{200}{500} \ll 1$  ← But, low frequency is dominant  $\int_0^{\infty} \omega J(\omega) \coth\left(\frac{\omega}{2kT}\right) d\omega$ ,  
 $\frac{kT}{\omega} \gg 1$  so the "high temperature" approximation is actually pretty good!

Spectral Density:

$$J(\omega) = \frac{1}{2} \hbar \omega^2$$

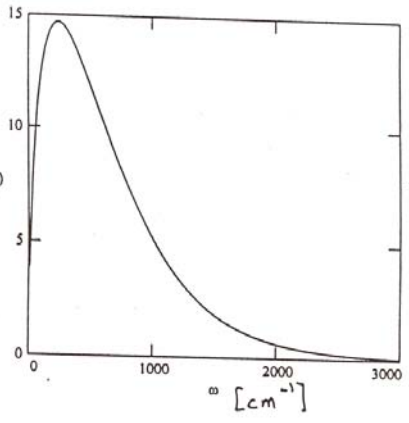


Fig. 1: Spectral Density [subohmic, S = 0.6,  $\omega_c = 400 \text{ cm}^{-1}$ ]

Golden Rule Time kernel:

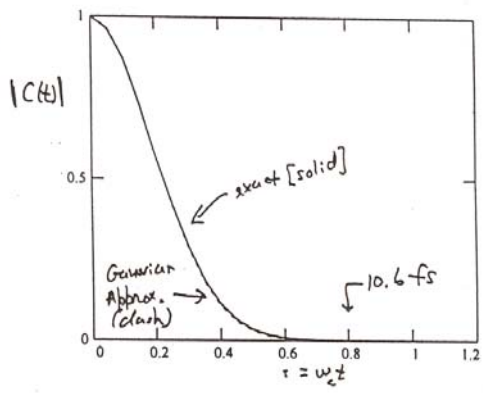


Fig. 2: Comparing  $C(t)$  to Gaussian approximation

Golden Rule Rate Constant vs. Bias (Reaction free energy)

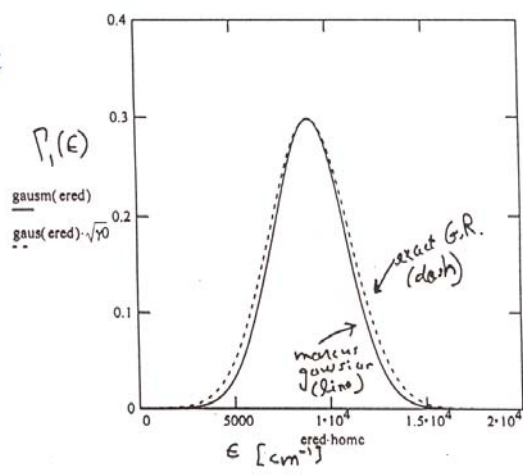


Fig. 3: Exact golden rule vs. Marcus rate constants.

(13)  
Supplemental Notes on the Externally (Sinusoidally) Driven Spin-Boson Model

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \quad \leftarrow \text{Golden Rule Analysis}$$

$$\text{w/ } |\psi(t)\rangle = |\varphi_D(x,t)\rangle |D\rangle + |\varphi_A(x,t)\rangle |A\rangle$$

$$\text{and: } \hat{H}(t) = |D\rangle\langle D| \{ \hat{h}_D - \mu E_0 \cos \omega_0 t \} + |A\rangle\langle A| \{ \hat{h}_A + \mu E_0 \cos \omega_0 t \} \leftarrow \hat{H}_0(t)$$

$$+ \Delta \{ |A\rangle\langle D| + |D\rangle\langle A| \} \quad \leftarrow \hat{V} \text{ (perturbation)}$$

Given:  $|\psi(0)\rangle = |\varphi_D^0(x)\rangle |D\rangle$ , use t.d. perturbation theory to  
 compute electronic state population  
 at time  $t$ :  
 nuclear coordinate eigenfnct. of  $h_D$   $\uparrow$  Donor

Find:

$$P_D(t) = 1 - \Delta^2 \frac{2}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' e^{-2i\omega_0 t'} e^{2i\omega_0 t''} \langle \varphi_D^0 | e^{i\hat{h}_D t'} e^{-i\hat{h}_A(t'-t'')} e^{-i\hat{h}_D t''} | \varphi_D^0 \rangle + \mathcal{O}(\Delta^4)$$

↑ Donor electronic state population

Pause: ... inverse temperature =  $\beta$   
 If consider a Boltzmann weighted distribution of nuclear coordinate eigenstates of electronic state  $|D\rangle$ , then ...

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$$P_D(t) = 1 - \Delta^2 \cdot 2 \operatorname{Re} \int_0^t dt' \int_0^{t'} dt'' e^{-2i a \sin \omega_0 t'} e^{2i a \sin \omega_0 t''}$$

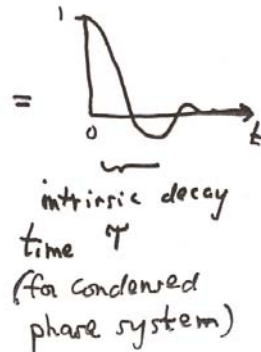
$$\operatorname{tr}_x \left\{ \hat{\rho}_D^A \hat{\rho}_D^B e^{i \hat{h}_D t'} e^{-i \hat{h}_D (t' - t'')} e^{-i \hat{h}_D t''} \right\} + O(\Delta^4)$$

↑  
thermal density operator for  $\hat{h}_D$

Now analyze:

$$\operatorname{tr}_x \left\{ \hat{\rho}_D^A \hat{\rho}_D^B e^{i \hat{h}_D t'} e^{-i \hat{h}_D (t' - t'')} e^{-i \hat{h}_D t''} \right\} =$$

$$\operatorname{tr}_x \left\{ \hat{\rho}_D^A e^{-i \hat{h}_D (t' - t'')} \hat{\rho}_D^B e^{i \hat{h}_D (t' - t'')} \right\} = G(t' - t'')$$



Thus:

$$P_D(t) = 1 - 2\Delta^2 \operatorname{Re} \sum_{n,m=-\infty}^{\infty} J_m(2a) J_n(2a) \cdot$$

$$\int_0^t dt' \int_0^{t'} dt'' e^{-im\omega_0 t'} e^{in\omega_0 t''} G(t' - t'')$$

only  $n=m$  makes contribution for  $\Delta/\omega_0 \ll 1$

$$e^{i(n-m)\omega_0 t'}$$

$$e^{-in\omega_0 (t' - t'')}$$

constant for  $t' \gg \tau$  (indep. of  $t'$ )

(15)

Finally:  $P_D(t) = 1 - K_{D \rightarrow A} t + O(\Delta^4)$

4)  $K_{D \rightarrow A}$  = rate of  $D \rightarrow A$  transition =

$$\Delta^2 \sum_{m=-\infty}^{\infty} J_m^2(2a) \cdot 2 \operatorname{Re} \int_0^{\infty} dt G'(t) e^{-im\omega_0 t}$$

Fractal-Coulomb spectrum at  
transform variable  $m\omega_0$



## NIBA for an Externally Driven Spin-Boson Model:

### System population

dynamics is described by the following generalized master equation derived in Refs. [7, 26] and by different methods in Refs. [24, 25]:

$$\begin{aligned} \frac{dx(t)}{dt} &= -\Delta^2 \int_0^t dt_1 \sin[F(t) - F(t_1) - (\epsilon/\hbar)(t - t_1)] \sin[Q_1(t - t_1)] e^{-Q_2(t-t_1)} \\ &\quad - \Delta^2 \int_0^t dt_1 \cos[F(t) - F(t_1) - (\epsilon/\hbar)(t - t_1)] \cos[Q_1(t - t_1)] e^{-Q_2(t-t_1)} x(t_1) \end{aligned} \quad (9)$$

Here  $x(t)$  is the difference in electronic populations between reactant and product states and

$$F(t) = \frac{\mu_0}{\hbar} \int_0^t dt_1 E(t_1) = \frac{\mu_0 E_0}{\hbar \omega} \sin(\omega t) \quad (10)$$

The last equality in Eq. (10) is based on specialization to the monochromatic driving field indicated in Eq. (2), which shall concern us throughout the present work. The functions  $Q_1(t)$  and  $Q_2(t)$  in Eq. (9) are determined by the boson spectral density [23]

$$Q_1(t) = \frac{1}{\hbar \pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \sin(\omega t), \quad (11)$$

$$Q_2(t) = \frac{1}{\hbar \pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [1 - \cos(\omega t)] \coth\left(\frac{\hbar \omega}{2kT}\right), \quad (12)$$

where the spectral density function is defined as

$$J(\omega) = \frac{\pi}{2} \sum_i \frac{g_i^2}{m_i \omega_i} \delta(\omega - \omega_i). \quad (13)$$

← Note:  $g_i = \epsilon_i$  in Loggett SB Ham. Hamiltonian \*

In Eqs. (11-13)  $\omega$  represents the angular frequency of a harmonic oscillator in the bath. All relevant details of the bath are encoded in the temporal functions  $Q_{1,2}(t)$ . Thus there should be no confusion with our notation of the laser field angular frequency by the same symbol, i.e. everywhere else in the paper  $\omega$  refers to the angular frequency of the laser field.

\* See: NIBA case studies section