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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.

A Better derivation 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 $\rho(t) = e^{-iH_0 t}\,\rho_I(t)\,e^{iH_0 t}$; and $H_I(t) = e^{iH_0 t}\,V\,e^{-iH_0 t}$

then:

$$\frac{\partial \rho_I}{\partial t} = -i\,[H_I(t), \rho_I(t)] \qquad [1]$$

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

A formal solution is:

$$\rho_I(t) = \rho_0 - i\int_0^t dt'\,[H_I(t'), \rho_I(t')] \qquad [2]$$

Substitute [2] into [1]:

$$\boxed{\frac{\partial \rho_I}{\partial t} = -i\,[H_I(t), \rho_0] - \int_0^t dt'\,[H_I(t), [H_I(t'), \rho_I(t')]]} \qquad [3] \quad \text{(exact)}$$

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

$$H_0 = |1\rangle\langle 1|\,h_1 + |2\rangle\langle 2|\,h_2 \,; \qquad V = \left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)\,\Delta$$

$$H_I(t) = \left(|1\rangle\langle 2|\,e^{ih_1 t}e^{-ih_2 t} + |2\rangle\langle 1|\,e^{ih_2 t}e^{-ih_1 t}\right)\Delta$$

$$\hat{\rho}_0 = |1\rangle\langle 1|\,\underbrace{\frac{e^{-\beta h_1}}{Z_1}}_{\rho_{\beta,1}}$$

Apply $\langle\alpha|\cdots|\alpha\rangle \Rightarrow \frac{\partial}{\partial t}\langle\alpha|\rho_I(t)|\alpha\rangle = -\int_0^t \langle\alpha|\,[H_I(t), [H_I(t'), \rho_I(t')]]\,|\alpha\rangle\,dt'$; $\alpha = 1, 2$

NB: $\langle\alpha|\,H_I(t)\,\rho_0\,|\alpha\rangle = \langle\alpha|\,\rho_0\,H_I(t)\,|\alpha\rangle = 0$

Now examine:

$$\langle 1| \left[H_I(t), [H_I(t'), \rho_I(t')] \right] |1\rangle = \underbrace{H_I(t)}_{|1\rangle\langle 2| e^{ih_1 t} e^{-ih_2 t}} \{ \overbrace{H_I(t')}^{|2\rangle\langle 1| e^{ih_2 t'} e^{-ih_1 t'}} \rho_I(t') - \rho_I(t') \underbrace{H_I(t')}_{|2\rangle\langle 1| e^{ih_2 t'} e^{-ih_1 t'}} \} - \{ \overbrace{H_I(t')}^{|1\rangle\langle 2| e^{ih_1 t'} e^{-ih_2 t'}} \rho_I(t') - \rho_I(t') \overbrace{H_I(t')}^{|1\rangle\langle 2| e^{ih_1 t'} e^{-ih_2 t'}} \} \underbrace{H_I(t)}_{|2\rangle\langle 1| e^{ih_2 t} e^{-ih_1 t}} |1\rangle$$

$$= \{ e^{ih_1 t} e^{-ih_2(t-t')} e^{-ih_1 t'} \langle 1|\rho_I(t')|1\rangle - e^{ih_1 t} e^{-ih_2 t} \langle 2|\rho_I(t')|2\rangle e^{ih_2 t'} e^{-ih_1 t'}$$

$$- e^{ih_1 t'} e^{-ih_2 t'} \langle 2|\rho_I(t')|2\rangle e^{ih_2 t} e^{-ih_1 t} + \langle 1|\rho_I(t')|1\rangle e^{ih_1 t'} e^{-ih_2(t'-t)} e^{-ih_1 t} \} \Delta^2$$

Hermitian ⟷ these are hermitian adjoints

Further

$$\frac{1}{\Delta^2} \cdot tr_x\left[\langle 1| [\ ,[\ ,\ ]] |1\rangle \right] = 2Re\, tr_x \{ e^{ih_1 t} e^{-ih_2(t-t')} e^{-ih_1 t'} \langle 1|\rho_I(t')|1\rangle \}$$

$$- 2Re\, tr_x \{ e^{+ih_2 t} e^{-ih_1(t-t')} e^{-ih_2 t'} \langle 2|\rho_I(t')|2\rangle \}$$

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

$$(i)\ \frac{1}{\Delta^2} \cdot \frac{\partial}{\partial t} \underbrace{tr_x\{\langle 1|\rho_I(t)|1\rangle\}}_{P_1(t)} = - \int_0^\infty dt' \left[2Re\, tr_x \{ e^{ih_1 t} e^{-ih_2(t-t')} e^{-ih_1 t'} \langle 1|\rho_I(t')|1\rangle \} \right.$$

$$\left. - 2Re\, tr_x \{ e^{ih_2 t} e^{-ih_1(t-t')} e^{-ih_2 t'} \langle 2|\rho_I(t')|2\rangle \} \right]$$

(ii) analogously w/ $1 \leftrightarrow 2$

That is: $\hat{\rho}_I(t) = \hat{\rho}_{\beta,1} \cdot \hat{\rho}^S_I(t)$ ← 2x2 system density matrix

thermal density operator for surface 1 harmonic oscillators. in small Δ limit

Progress is made by assuming $\langle 1|\rho_I(t)|1\rangle \cong P_1(t)\, \rho_{\beta,1}$; $\langle 2|\rho_I(t)|2\rangle = P_2(t)\, \rho_{\beta,2}$

Also note: $tr_x\{ e^{ih_1 t} e^{-ih_2(t-t')} e^{-ih_1 t'} \rho_{\beta,1} \} = tr_x\{ e^{-ih_2(t-t')} e^{ih_1(t-t')} \rho_{\beta,1} \}$

Finally ...

$$(\ddagger)\quad \boxed{\begin{aligned} \frac{dp_1(t)}{dt} &= -\int_0^t dt' \left\{ \mathcal{K}_{2\leftarrow 1}(t-t')\,p_1(t') - \mathcal{K}_{1\leftarrow 2}(t-t')\,p_2(t') \right\} \\ \frac{dp_2(t)}{dt} &= -\int_0^t dt' \left\{ \mathcal{K}_{1\leftarrow 2}(t-t')\,p_2(t') - \mathcal{K}_{2\leftarrow 1}(t-t')\,p_1(t') \right\} \end{aligned}}$$

w

$$\boxed{\mathcal{K}_{2\leftarrow 1}(t) = \Delta^2\, 2\,\mathrm{Re}\,\mathrm{tr}_X \left\{ e^{-ih_2 t}\, e^{ih_1 t}\, \rho_{\beta,1} \right\}} \quad (\ddagger)$$

NB: Using projection operator techniques **, it can be shown that $\underline{\underline{\text{exact}}}$ $\underbrace{\text{generalized Master Eqs.}}_{\text{GME's}}$ of the form $(\ddagger)$ exist with

$$\mathcal{K}_{2\leftarrow 1}(t) = \Delta^2 \mathcal{K}^{(2)}_{2\leftarrow 1}(t) + \Delta^4 \mathcal{K}^{(4)}_{2\leftarrow 1}(t) + \ldots$$

the $\mathcal{K}$'s are independent of Δ

with

$$\mathcal{K}^{(2)}_{2\leftarrow 1}(t) = 2\,\mathrm{Re}\,\mathrm{tr}_X \left\{ e^{-ih_2 t}\, e^{ih_1 t}\, \rho_{\beta,1} \right\} \qquad [\text{exactly!}] \leftarrow \left[\begin{array}{l} \Delta^2 \mathcal{K}^{(2)}_{2\leftarrow 1}(t) \\ \text{same as } (\ddagger) \end{array} \right.$$

Thus "w/ $\Delta \to 0$, the GME's in $(\ddagger)$ become exact(!)" ← [one hopes!]

Practical Question: how small a value of Δ 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 the $\mathcal{O}(\Delta^2)$ term suffices!

** M. Sparpaglione + S. Mukamel, J. Chem. Phys. 88, 3263 (88);
Y. Hu + S. Mukamel, J. Chem. Phys. 91, 6973 (89).

More on the NIBA: Some Case Studies

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

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

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

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

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

with:

$$g(t) = \Delta^2 \cos(\epsilon t) \cos\left(\frac{1}{\pi}\varphi_1(t)\right) \exp\left\{-\frac{1}{\pi}\varphi_2(t)\right\}$$

$$h(t) = \Delta^2 \sin(\epsilon t) \sin\left(\frac{1}{\pi}\varphi_1(t)\right) \exp\left\{-\frac{1}{\pi}\varphi_2(t)\right\}$$

and:

$$\varphi_1(t) = \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \sin(\omega t)$$

$$\varphi_2(t) = \int_0^\infty d\omega \frac{J(\omega)}{\omega^2}\left[1 - \cos(\omega t)\right] \coth\left(\frac{\omega}{2kT}\right)$$

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 $P_1(0) = 1 \Rightarrow \sigma(0) = 1$

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

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

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

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

Ohmic bath: $J(\omega) = \eta\,\omega\, e^{-\omega/\omega_c}$; $\alpha \equiv \eta/2\pi$

consider $T=0$; $\varphi_1(t) = \eta \tan^{-1}(\omega_c t)$; $\varphi_2(t) = \frac{\eta}{2}\ln\left(1+(\omega_c t)^2\right)$

Or:

$$\boxed{g(t) = \frac{\Delta^2}{\omega_c}\frac{\cos\left[2\alpha \tan^{-1}(\omega_c t)\right]}{\left[1+(\omega_c t)^2\right]^{\alpha}}} \; ; \; T=0 \text{ ohmic}$$

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

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

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

$[T=0]$

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

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

$\alpha>1$ <u>Localization</u> (confidence)

At finite Temps : $0<\alpha<1$, $\alpha T \geq \Delta_r$ Exponential relaxation w rate $\propto T^{2\alpha-1}$ (See Legg.)

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

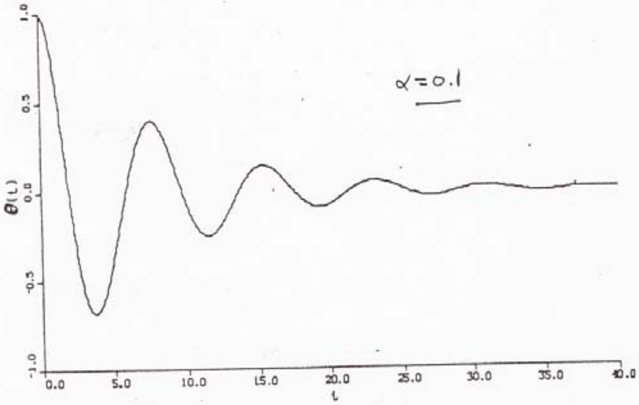
$T>0$; Expo. relaxation w rate $\propto e^{-(T_0/T)^{1-s}}$ (See Legg.)

// Superohmic case :

$1<s<2$ damped oscillations at $T=0$; exponential relaxation for $T>T^*$ (See Legg.)

$s>2$ Exponentially damped sinusoidal oscillation $\Theta(t)=\cos\tilde{\Delta}t\ e^{-Kt}$ (adiabatically renormalized tunnelling constant)

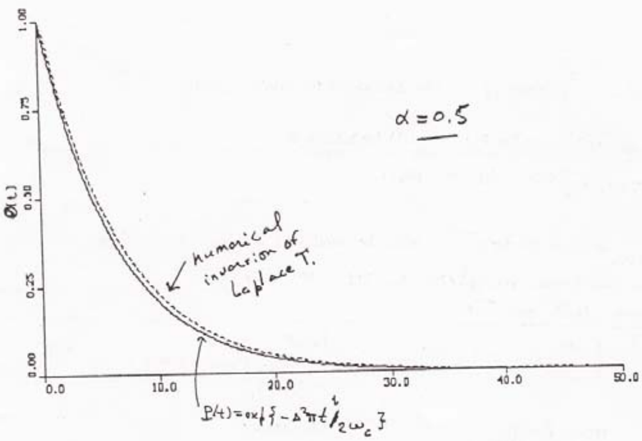
$K \sim K_{\text{golden rule}}$

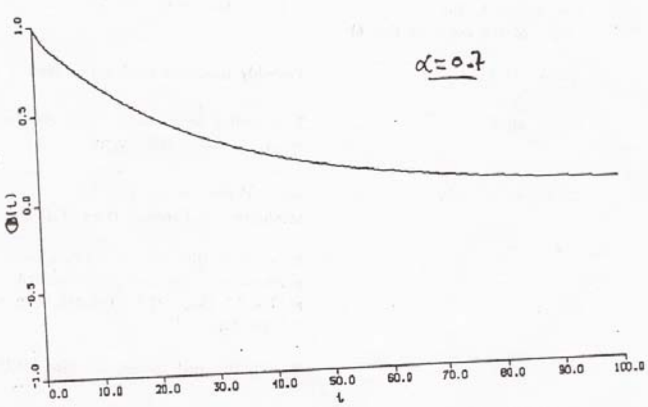


Ohmic Spectral Density

$$J(\omega) = \eta \omega e^{-\omega/\omega_c}$$

$$\left[\alpha = \eta/2\pi\right]$$





} nonexponential (algebraic) decay

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

8

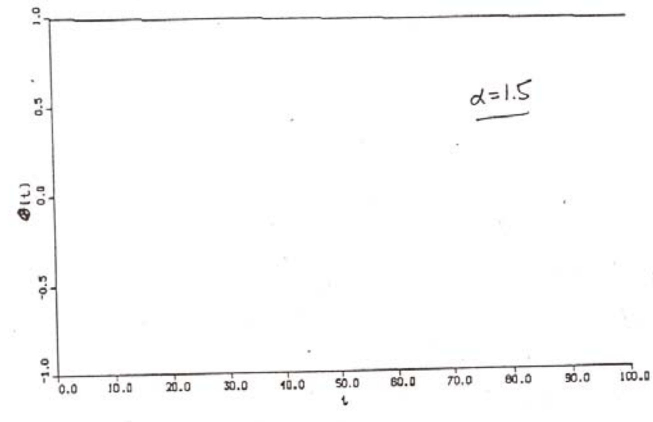


TABLE I. Summary of results for $P(t)\equiv\langle\sigma_z(t)\rangle$ for bias $\epsilon=0$.

$$H=-\tfrac{1}{2}\hbar\Delta\sigma_x+\tfrac{1}{2}q_0\sigma_z\sum_\alpha C_\alpha x_\alpha+H_b(\{m_\alpha\},\{\omega_\alpha\}),$$

$$J(\omega)\equiv\frac{\pi}{2}\sum_\alpha\frac{C_\alpha^2}{m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha)\doteq A\omega^s e^{-\omega/\omega_c}$$ with the conditions $\Delta\ll\omega_c,\ k_BT\ll\hbar\omega_c$.

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

$0<s<1$	$T=0$	Localization
	$T\neq0$	exponential relaxation with a rate $\propto\exp[-(T_0/T)^{1-s}]$ (Sec. VI.A)
$s=1$ (ohmic)	$\alpha>1,\ T=0$	Localization
	$\alpha>1,\ T\neq0$ or $\alpha<1,\ \alpha T\gtrsim\Delta_r$ (i.e., region to the right of the curve in Fig. 8)	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)
	$\alpha=\frac{1}{2}$, 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 $\epsilon\neq0$, see Sec. VII.

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 "P_1, P_2" form:

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

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

with:

$$\mathcal{K}_{2\leftarrow 1}(t) = \frac{\Delta^2}{2} e^{-\frac{Q_2(t)}{\pi}} \cos\left[\frac{Q_1(t)}{\pi} + \epsilon t\right]$$

$$\mathcal{K}_{1\leftarrow 2}(t) = \frac{\Delta^2}{2} e^{-\frac{Q_2(t)}{\pi}} \cos\left[\frac{Q_1(t)}{\pi} - \epsilon t\right]$$

[Note connection to "σ" form: $\sigma = P_1 - P_2$; $1 = P_1 + P_2 \Rightarrow \mathcal{K}_{2\leftarrow 1} = \frac{g-h}{2}$;
$\mathcal{K}_{1\leftarrow 2} = \frac{g+h}{2}$]

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:

$$k_{2\leftarrow 1} = \frac{\Delta^2}{2}\int_0^\infty dt\, e^{-\frac{Q_2(t)}{\pi}} \cos\left(\frac{Q_1(t)}{\pi} + \epsilon t\right) = \frac{\Delta^2}{4}\int_{-\infty}^{\infty} dt\, e^{-\frac{Q_2(t)}{\pi}}\, e^{\frac{iQ_1(t)}{\pi} + i\epsilon t}$$

$$k_{1\leftarrow 2} = \frac{\Delta^2}{2}\int_0^\infty dt\, e^{-\frac{Q_2(t)}{\pi}} \cos\left(\frac{Q_1(t)}{\pi} - \epsilon t\right) = \frac{\Delta^2}{4}\int_{-\infty}^{\infty} dt\, e^{-\frac{Q_2(t)}{\pi}}\, e^{\frac{iQ_1(t)}{\pi} - i\epsilon t}$$

Now make the "short-time" approximation: ← Validity requires $\omega_c t_{decay} \ll 1$

$$\frac{\varphi_1(t)}{\pi} = \frac{1}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \underbrace{\sin(\omega t)}_{[\omega t + \dots]} \cong t \cdot \underbrace{\boxed{\frac{1}{\pi}\int_0^\infty d\omega\, J(\omega)/\omega}}_{E_r}$$

$$\frac{\varphi_2(t)}{\pi} = \frac{1}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \underbrace{[1-\cos(\omega t)]}_{\omega^2 t^2/2 + \dots} \coth\left(\frac{\omega}{2kT}\right) = t^2 \cdot \frac{1}{2\pi}\int_0^\infty d\omega\, J(\omega) \coth\left(\frac{\omega}{2kT}\right)$$

Further "progress" w/ $\varphi_2(t)$ is obtained by making high temperature approximation: $\frac{\omega}{kT} \ll 1$

Then: $$\frac{\varphi_2(t)}{\pi} \cong t^2 \cdot \frac{1}{2\pi}\int_0^\infty d\omega\, J(\omega)\left[\frac{2kT}{\omega}\right] = t^2 \cdot kT \cdot \underbrace{\boxed{\frac{1}{\pi}\int_0^\infty d\omega\, J(\omega)/\omega}}_{E_r}$$

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

Now:

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

Similarly:

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

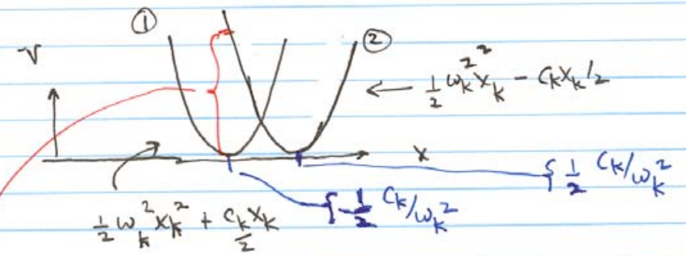
Final details of Marcus Theory:

1) What is E_r?:

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

← (multimode) reorganization energy

Look at displacements in one phonon coordinate:



$\underbrace{\quad}_{c_k/\omega_k^2}$ ← net equilibrium shift from state ① ↔ ②

$$\frac{1}{2}\omega_k^2 \left[c_k/\omega_k^2\right]^2 = \frac{1}{2}\frac{c_k^2}{\omega_k^2} = \text{single mode reorganization energy}$$

2) Consistency checks: for polar electron transfer $E_r \cong 1\,eV$;

$$\omega_c \sim 500\,cm^{-1}; \quad kT \cong 200\,cm^{-1}$$

i) $$(\omega_c t_{decay})^2 \cong \omega_c^2 \cdot \frac{1}{E_r kT} \cong \frac{(500\,cm^{-1})^2}{(8000\,cm^{-1})(200\,cm^{-1})} = \frac{25}{16} \times 10^{-1} \ll 1$$

ii) $\frac{kT}{\omega_c} = \frac{200}{500} \not\gg 1$ ← But, low frequencies dominate $\int_0^\infty d\omega \, J(\omega) \coth\left(\frac{\omega}{2kT}\right)$,

$\frac{kT}{\omega} \gg 1$

so the "high temperature" approximation is actually pretty good(!)

Spectral Density:

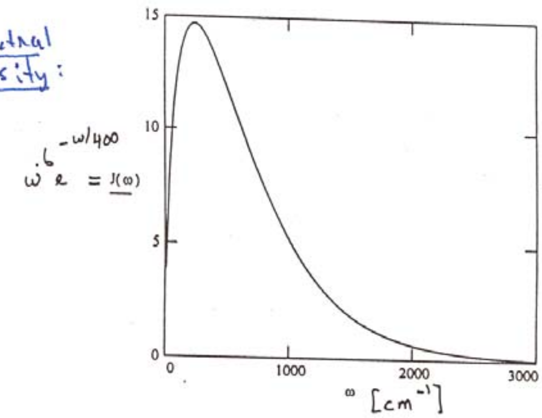


Fig. 1: Spectral Density [subohmic, $s = 0.6$, $\omega_c = 400$ cm^{-1}]

Golden Rule Time kernel:

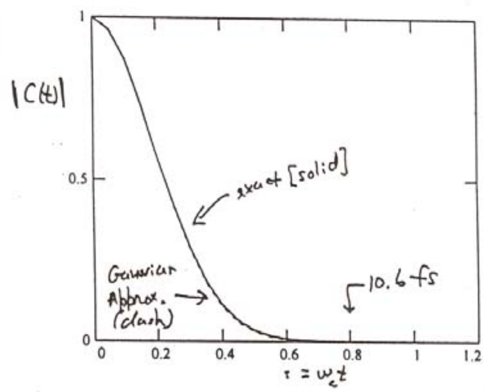


Fig. 2: Comparing C(t) to Gaussian approximation

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

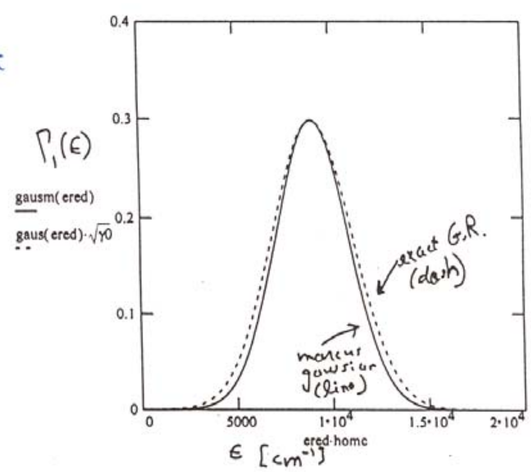


Fig. 3: Exact golden Rule vs. marcus rate constants.

(13')

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

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$$ ← Golden Rule Analysis

w/ $|\Psi(t)\rangle = |\varphi_D(x,t)\rangle|D\rangle + |\varphi_A(x,t)\rangle|A\rangle$

and:

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

$$+\,\Delta\{|A\rangle\langle D| + |D\rangle\langle A|\}$$ ← $\hat{V}$ (perturbation)

Given: $|\Psi(0)\rangle = |\varphi_D^0(x)\rangle|D\rangle$, use t.d. perturbation theory to compute Donor electronic state population at time t:

nuclear coordinate eigenfunct. of $\hat{h}_D$

Find:

$$P_D(t) = 1 - \Delta^2 2\mathrm{Re}\int_0^t dt'\int_0^{t'} dt''\, e^{-2ia\sin\omega_0 t'}\, e^{2ia\sin\omega_0 t''} \cdot \langle\varphi_D^{(0)}(x)|e^{i\hat{h}_D t'}\, e^{-i\hat{h}_A(t'-t'')}\, e^{-i\hat{h}_D t''}|\varphi^0(x)\rangle + O(\Delta^4)$$

Donor electronic state population

Pause...

If consider a Boltzmann weighted distribution of nuclear coordinate eigenstates of electronic state $|D\rangle$, then...

inverse temperature $= \beta$

$$P_D(t) = 1 - \Delta^2 \cdot 2\,\mathrm{Re} \int_0^t dt' \int_0^{t'} dt'' \; e^{-2ia\sin\omega_0 t'} \; e^{2ia\sin\omega_0 t''}$$

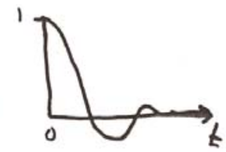
$$\mathrm{tr}_x\{\hat\rho_D^\beta \, e^{i\hat h_D t'} \, e^{-i\hat h_A(t'-t'')} \, e^{-i\hat h_D t''}\} + O(\Delta^4)$$

$\uparrow$ thermal density operator for $\hat h_D$

<u>Now</u> <u>analyze</u>:

$$\mathrm{tr}_x\{\hat\rho_D^\beta \, e^{i\hat h_D t'} \, e^{-i\hat h_A(t'-t'')} \, e^{-i\hat h_D t''}\} =$$

$$\mathrm{tr}_x\{\hat\rho_D^\beta \, e^{-i\hat h_A(t'-t'')} \, e^{i\hat h_D(t'-t'')}\} = C(t'-t'') =$$



intrinsic decay time τ
(for condensed phase system)

<u>Thus</u>:

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

$$\int_0^t dt' \left[\int_0^{t'} dt'' \, \underbrace{e^{-im\omega_0 t'} \, e^{in\omega_0 t''}} \, C(t'-t'') \right]$$

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

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

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

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

w/ $k_{D\to A}$ = rate of $D\to A$ transitions =

$$\boxed{\Delta^2 \sum_{m=-\infty}^{\infty} J_m^2(2a) \cdot \underbrace{2\,\mathrm{Re} \int_0^\infty d\tau\, G(\tau)\, e^{-im\omega_0\tau}}_{}}$$

Franck-Condon spectrum at transform variable $m\omega_0$

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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]:

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

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 : $g_i = C_i$ in Leggett SB Hamiltonian *

In Eqs. (11-13) ω 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 ω refers to the angular frequency of the laser field.

* See: NIBA case studies section