The Spin-Boson Model, Part I.

Topics covered:

1) Statement of the Hamiltonian.

2) Connecting the Spin-Boson Hamiltonian to Physical Problems:

i) Multidimensional Tunneling
ii) Electron-Phonon Coupling in Solids and Liquids

3) Quantum Dynamics of the Spin-Boson Model (in the weak-tunneling regime): What are the appropriate initial conditions and quantities of interest (the reduced system density matrix)?

4) Short-time Dynamics: the Fermi Golden Rule

5) The Quest for Long-time Dynamics: constructing time-local kinetic master equations (gain-loss equations) that utilize Golden Rule rate constants.

6) Evaluation of Golden-Rule time-kernels and rate constants for the Spin-Boson model (Linearly Displaced Harmonic Oscillators).

7) References

Aug. 04,

The Spin-Boson Model of Condensed Phase (System - Bath)

Quantum Dynamics

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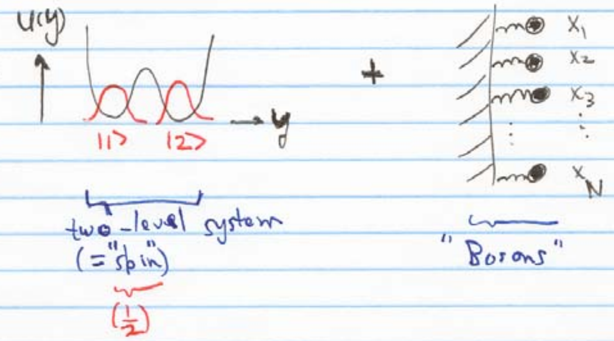
The (super)system :



The Spin-Boson Hamiltonian (and corresponding state space) :

$$H = \begin{pmatrix} \epsilon & \Delta \\ \Delta & -\epsilon \end{pmatrix} + \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 x_j^2 \right) + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \sum_j \lambda_j x_j$$

$$= |1\rangle\langle 1| \left\{ \epsilon + \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 x_j^2 + \lambda_j x_j \right) \right\} + |2\rangle\langle 2| \left\{ -\epsilon + \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 x_j^2 - \lambda_j x_j \right) \right\}$$

$$+ \Delta \left(|1\rangle\langle 2| + |2\rangle\langle 1| \right)$$

$$= |1\rangle\langle 1| \left\{ \epsilon + \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left[x_j + \frac{\lambda_j}{\omega_j^2}\right]^2 \right) \right\} + |2\rangle\langle 2| \left\{ -\epsilon + \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left[x_j - \lambda_j/\omega_j^2\right]^2 \right) \right\}$$

$$+ \Delta \left(|1\rangle\langle 2| + |2\rangle\langle 1| \right) - \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}_{(|1\rangle\langle 1| + |2\rangle\langle 2|)} \cancel{\sum_j} \lambda_j^2 / 2\omega_j^2$$

irrelevant overall shift constant

For the initial (density matrix) state, typically: $\hat{\Gamma}(0) = |1\rangle\langle 1| \hat{\rho}_X(0)$

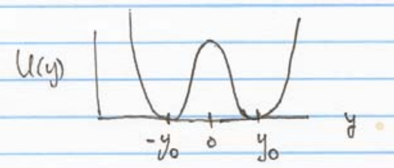
with (typically): $$\hat{\rho}_X(0) = e^{-\beta\hat{h}_1} / \mathrm{tr}_X\left(e^{-\beta\hat{h}_1}\right) ; \quad \hat{h}_1 = \sum_j \left(\hat{P}_j^2/2 + \frac{1}{2}\omega_j^2 \left[X_j + \lambda_j/\omega_j^2\right]^2 \right)$$

Physical Underpinnings of the Spin-Boson model:

(I) Multidimensional Tunneling

Consider (for simplicity) a tunneling coordinate, y, coupled to one harmonic oscillator coordinate, X.

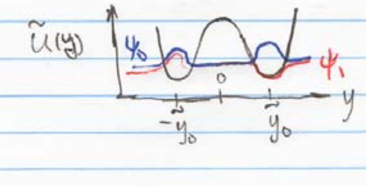
let the "bare" tunneling potential $U(y)$



Then, let:

$$V(x,y) = U(y) + \frac{1}{2}\omega^2\left(x + \lambda y/\omega^2\right)^2$$
$$= \underbrace{U(y) + \lambda^2 y^2/2\omega^2}_{\tilde{U}(y)} + \lambda y x + \frac{1}{2}\omega^2 x^2$$

Now, consider the "renormalized" 1-d tunneling potential $\tilde{U}(y)$:



Find (numerically) the eigenfunctions ψ_0, ψ_1, and energy the corresponding energy levels E_0, E_1 of $\tilde{U}$

Now exchange $\psi_{0,1}$ for Left and Right localized linear combinations

$$\psi_L(y) = \frac{1}{\sqrt{2}}\left(\psi_0(y) + \psi_1(y)\right) \quad ; \quad \psi_R(y) = \frac{1}{\sqrt{2}}\left(-\psi_0(y) + \psi_1(y)\right)$$

Next, take matrix elements of the (2-d) supersystem Hamiltonian in the $|L\rangle, |R\rangle$ basis :

$$H = \underbrace{\left[\frac{p_y^2}{2} + \tilde{U}(y)\right]}_{h_y} + \left[\frac{p_x^2}{2} + \frac{1}{2}\omega^2 x^2\right] + \lambda y x$$

$\langle L|$ $\qquad$ $|R\rangle$

Note:

$$\langle R|h_y|R\rangle = \frac{1}{\sqrt{2}}\left(\langle\psi_0| + \langle\psi_1|\right)\hat{h}_y\left(|\psi_0\rangle + |\psi_1\rangle\right)\frac{1}{\sqrt{2}} = \frac{E_0+E_1}{2} \equiv \tilde{E}$$

Similarly:

$$\langle L|h_y|L\rangle = \tilde{E} \quad ; \quad \langle L|h_y|R\rangle = \langle R|h_y|L\rangle = \frac{E_1-E_0}{2} \equiv \Delta$$

Furthermore: $\langle L|\,y\,|L\rangle \cong -\tilde{y}_0$; $\langle R|\,y\,|R\rangle \cong \tilde{y}_0$

and : $\langle R|\,y\,|L\rangle = 0 = \langle L|\,y\,|R\rangle$ [by symmetry]

Thus: In the $|L,R\rangle$ basis,

$$H = \underbrace{\begin{pmatrix} \bar{E} & \Delta \\ \Delta & \bar{E} \end{pmatrix}}_{\cancel{\bar{E}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}} + \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix}} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\left[p_x^2/2 + \frac{1}{2}\omega_j^2 x_j^2\right] - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\tilde{y}_0 \lambda x$$

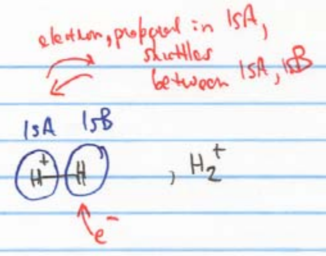
← of (symmetric) $\underbrace{\text{Spin-Boson}}_{SB}$ form

irrelevant overall, constant shift

N.B.: extension to asymmetric SB case, and to multi-oscillator bath, is straightforward

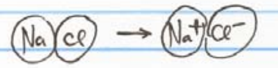
(II) Electron - Phonon Coupling

Consider 1st an isolated charge transfer system; e.g.:

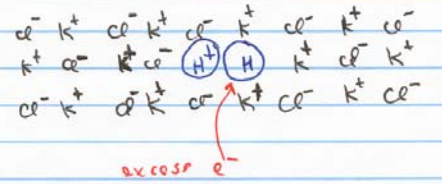


, H_2^+

or :



Now embed this molecular 2-state electron transfer system in the lattice of an ionic crystal



There is an interaction energy between the shuttling (tunneling) electron and the lattice ions due to electrostatic forces.

$$V_{int}(\vec r_j; \underbrace{\vec x_1, \dots, \vec x_N}_{\text{lattice atoms}}) = -\sum_{j=1}^{N} \frac{e_0 q_j}{|\vec r - \vec x_j|}$$

tunneling electron

; e_0 = proton charge;

q_j = charge on lattice ion j $= \begin{cases} e_0 \text{ for } K^+ \\ -e_0 \text{ for } Cl^- \end{cases}$

Letting: $\vec x_j = \vec x_j^{eq} + \underbrace{\Delta \vec x_j}_{\text{phonon displacement coordinate(s) for lattice ion } j.}$

Clearly, one can expand V_{int} in the phonon displacement coordinates.

$$V_{int}(\vec r; \underbrace{\vec x_1, \dots, \vec x_N}_{\equiv \vec X}) = V_{int}(r, \vec X_{eq}) + \sum_j \frac{\partial V_{int}}{\partial \vec x_j}\Big|_{\vec X_{eq}} \cdot \Delta \vec x_j + \underbrace{\cdots}_{\text{quadratic and higher order in phonon displacements}}$$

function of $\vec r$ (only)

Thus, denoting $\vec{\Delta X}_j \to x_j$ ← phonon displacements (one for each Cartesian component of each atom in the crystal lattice)

$$H = \frac{p_{\vec r}^2}{2} + \mathcal{U}_0(\vec r) + V_{int}(\vec r, \vec X_{eq}) + \sum_j f_j(\vec r)\, x_j + \underbrace{\sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 x_j^2 \right)}_{\text{adopt}}$$

↑ isolated H_2^+ potential experienced by its electron

↑ gradient coefficients

adopt Einstein model of lattice vibrations, for simplicity

combine these into a net 1-electron potential ← use this to determine $\widetilde{1sA}(\vec r) \to$ "$|L\rangle$" and $\widetilde{1s_B}(\vec r) \to$ "$|R\rangle$" base states

1-electron

Compute $\langle L,R | H | L,R \rangle \Rightarrow$

$$H = \begin{pmatrix} \epsilon & \Delta \\ \Delta & -\epsilon \end{pmatrix} + \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 x_j^2 \right) + \begin{pmatrix} \sum_j f_j^{LL} x_j & \sum_j f_j^{LR} x_j \\ \sum_j f_j^{RL} x_j & \sum_j f_j^{RR} x_j \end{pmatrix} \qquad (*)$$

↑ for H_2^+ in ~~an~~ (otherwise) isotropic crystal, $\epsilon = 0$

where: $\langle L | f_j(\vec r) | R \rangle = f_j^{LR}$, etc. ; note $f_j^{LR} = f_j^{RL}$

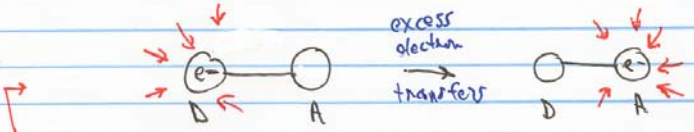
Finally, assume $f_j^{LR} \cong 0$ due to "exponentially small overlap between $\widetilde{1s}_A(\vec r)$ and $\widetilde{1s}_B(\vec r)$" ["Condon approximation"]

Then (*) is of Spin-boson form (!)

N.B.: The shifts in phonon equilibrium positions (in this S.B. Hamiltonian are) a direct consequence of electrostatically induced distortion of the crystal lattice (which differs when the excess e^- is in $|L\rangle$ or $|R\rangle$)

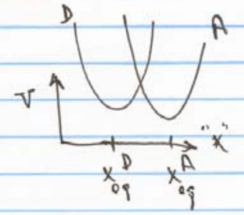
N.B.:

A related system which can be described by a Spin-Boson Hamiltonian is: molecular electron transfer in a polar fluid.



solvent dipoles
reorganize after
the excess electron transfers

Thus the idea of:



is suggested

solvent has different equilibrium configuration in D vs. A states.
electronic

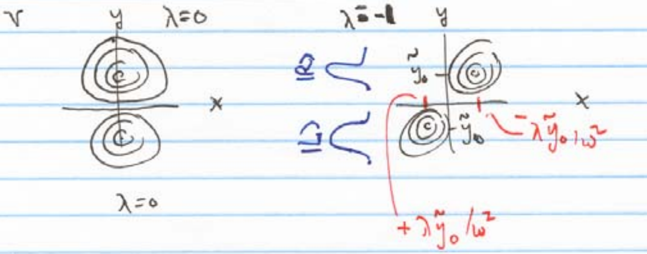
However: Clearly, there is no applicable linear expansion of nuclear coordinates about a single mechanical equilibrium configuration. Thus the derivation of a Spin-Boson model of electron transfer in a polar fluid is more subtle.
[This is the subject of linear response theory and Marcus theory.]

Moving on to ...
Dynamics under the Spin-Boson model.

First: 1) What are the appropriate initial conditions?

2) What properties do we want to calculate?

For concreteness, consider mult-d tunneling case: Illustrating in 2-d (one oscillator)



At $t=0$,
prepare a <u>local</u> equilibrium in the $|L\rangle$ state.

At $T=0$, $\Psi_0(x,y) \cong \Psi_L(y)\,\phi_0(x)$, where $\Big[\underbrace{\frac{p_x^2}{2} + \frac{1}{2}\omega^2(x - \tilde{y}_0\lambda/\omega^2)^2}_{\hat{h}_L}\Big]\phi_0(x) = \frac{\omega}{2}\phi_0(x)$ ← vibrational ground state

Thus the finite temperature analog is: $\boxed{\hat{\Gamma}(0) = |L\rangle\langle L|\, \frac{e^{-\beta\hat{h}_L}}{\mathrm{tr}_x(e^{-\beta\hat{h}_L})}}$

The main quantity of interest is:

$$\mathrm{tr}_x\{\hat{\Gamma}(t)\} = \hat{\rho}_s(t)$$ ← (2x2) system reduced density matrix

In particular, $\langle\alpha|\hat{\rho}_s(t)|\alpha\rangle$ = probability of being in $\alpha = L, R$ part of the multi-d tunneling potential (regardless of precise position of the oscillator coordinates).

So ... how do we calculate $\hat{\rho}_s(t)$???

Consider the case that Δ is small ; use (Fermi) Golden Rule to evaluate short-time dynamics

$\uparrow$ bare tunnel matrix element

For convenience, write the SB Hamiltonian in the following form:

$$H_{SB} = \begin{bmatrix} h_1 & \Delta \\ \Delta & h_2 \end{bmatrix} ; \quad \hat{h}_1 = \sum_j \left(\frac{P_j^2}{2} + \frac{1}{2}\omega_j^2 \left[x_j + \lambda_j/\omega_j^2\right]^2 \right) + \epsilon$$

$$\hat{h}_2 = \sum_j \left(\frac{P_j^2}{2} + \frac{1}{2}\omega_j^2 \left[x_j - \lambda_j/\omega_j^2\right]^2 \right) - \epsilon$$

Again, the initial supersystem density matrix is: $\hat{\rho}(0) = |1\rangle\langle 1| \dfrac{e^{-\beta h_1}}{tr_{\mathbf{x}}\{\exp(-\beta h_1)\}} \leftarrow Z_1$

Calculate the short-time evolution of the initial state $|1\rangle|\varphi_0\rangle$

$\uparrow$ arbitrary spatial wavepacket in $\vec{x}$-space

$$P_1(t) = \langle\varphi_0|\langle 1| e^{iH_{SB}t} \underline{|1\rangle\langle 1| e^{-iH_{SB}t} |1\rangle|\varphi_0\rangle}$$

component of $\varphi_0(\vec{x})$ that remains on diabatic surface 1

Partition H_{SB} as:
$$H_{SB} = \underbrace{|1\rangle\langle 1|\hat{h}_1 + |2\rangle\langle 2|\hat{h}_2}_{H_0} + \underbrace{\Delta\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)}_{V}$$

Then:
$$e^{-iH_{SB}t} = e^{-iH_0 t}\left\{1 - i\int_0^t dt'\, \hat{V}(t') - \int_0^t dt' \int_0^{t'} dt''\, V(t')\,V(t'') + \cdots\right\}$$

with
$$\hat{V}(t) = e^{iH_0 t}\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)e^{-iH_0 t}\cdot\Delta = \Delta\left(|1\rangle\langle 2|\, e^{ih_1 t}\, e^{-ih_2 t} + |2\rangle\langle 1|\, e^{ih_2 t}\, e^{-ih_1 t}\right)$$

Now:
$$\langle 1|e^{-iH_{SB}t}|1\rangle = e^{-ih_1t}\Big(1-\int_0^t dt'\int_0^{t'}dt''\langle 1|\underbrace{V(t')}_{\Delta\left(|1\rangle\langle 2|\,e^{ih_1t'}e^{-ih_2t'}+|2\rangle\langle 1|\,e^{ih_2t'}e^{-ih_1t'}\right)}\underbrace{V(t'')}_{\Delta\left(|1\rangle\langle 2|\,e^{ih_1t''}e^{-ih_2t''}+|2\rangle\langle 1|\,e^{ih_2t''}e^{-ih_1t''}\right)}|1\rangle+\overset{\mathcal{O}(\Delta^4)}{\dots}\Big)$$

Or:
$$\langle 1|e^{-iH_{SB}t}|1\rangle = e^{-ih_1t}\Big(1-\Delta^2\int_0^t dt'\int_0^{t'}dt''\,e^{ih_1t'}\underbrace{e^{-ih_2t'}\,e^{ih_2t''}}_{e^{-ih_2(t'-t'')}}\,e^{-ih_1t''}\quad+\dots\Big)$$

Thus:
$$P_1(t)\cong\langle\varphi_0|\Big(1-\Delta^2\int_0^t dt'\int_0^{t'}dt''\,e^{ih_1t''}\,e^{+ih_2(t'-t'')}\,e^{-ih_1t'}\Big)\,\cancel{e^{ih_1t}}\,\cdot$$
$$\cancel{e^{-ih_1t}}\Big(1-\Delta^2\int_0^t dt'\int_0^{t'}dt''\,e^{ih_1t'}\,e^{-ih_2(t'-t'')}\,e^{-ih_1t''}\Big)|\varphi_0\rangle$$

$$=1-\Delta^2\cdot 2\mathrm{Re}\int_0^t dt'\int_0^{t'}dt''\langle\varphi_0|e^{ih_1t'}e^{-ih_2(t'-t'')}\,e^{-ih_1t''}|\varphi_0\rangle$$

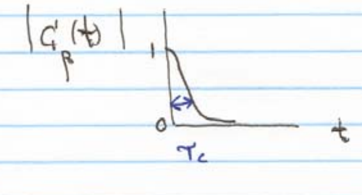
For the case of direct interest here, $\varphi_0(\vec{x}) = \varphi_1^{(j)}(\vec{x})$ s.t. $\hat{h}_1\varphi_1^{(j)}(\vec{x}) = \epsilon_1^{(j)}\varphi_1^{(j)}(\vec{x})$

Now:
$$P_1(t) = 1-\Delta^2\cdot 2\mathrm{Re}\int_0^t dt'\int_0^{t'}dt''\,G^{(j)}(t'-t'')\quad;\quad\boxed{G^{(j)}(\tau)\equiv e^{i\epsilon_1^{(j)}\tau}\langle\varphi_1^{(j)}|e^{-ih_2\tau}|\varphi_1^{(j)}\rangle}$$

Finally, consider the finite temperature analog:
$$P_1(t) = \mathrm{tr}_x\langle 1|\hat{\rho}(t)|1\rangle = \int d\vec{x}\,\langle 1|e^{-iH_{SB}t}|1\rangle\frac{|\varphi_1^{(j)}\rangle\langle\varphi_1^{(j)}|}{Z_1}e^{-\beta\epsilon_1^{(j)}}\,e^{iH_{SB}t}|1\rangle$$
$$\cong 1-\Delta^2\cdot 2\mathrm{Re}\int_0^t dt'\int_0^{t'}dt''\,G_\beta(t'-t'')$$

w/ $$\boxed{G^1_\beta(\tau)} = \frac{\sum_j e^{-\beta \epsilon_1^{(j)}} G^j(\tau)}{Z_1} = \boxed{tr_x \{ \hat{\rho}_{\beta,1} e^{ih_1\tau} e^{-ih_2\tau} \}} \; ; \; \hat{\rho}_{\beta,1} = \frac{e^{-\beta h_1}}{Z_1}$$

It can be shown, by direct evaluation of $G^1_\beta(t)$ for $\hat{h}_{1,2}$ corresponding to the Spin Boson model, that in many cases (particularly when the electron-phonon coupling is large);



← $G_\beta(t)$ decays to 0 on a finite time scale τ_c (which is independent of the hopping matrix Δ)

If so, then for small Δ :

$$\Delta^2 \cdot 2\mathrm{Re} \int_0^{t'} dt'' \, G^1_\beta(t'-t'') \underset{t' \gg \tau_c}{=} \Delta^2 \cdot 2\mathrm{Re} \int_0^{\infty} du \, G^1_\beta(u) = \Delta^2 \int_{-\infty}^{\infty} du \, G^1_\beta(u) \equiv K_{2\leftarrow 1}$$

Then: $P_1(t) \cong 1 - K_{2\leftarrow 1} t \quad ; \quad P_2(t) \cong K_{2\leftarrow 1} t$

Is this info useful for computing <u>long</u>-time dynamics of the SB model?

... In many cases (relevant to chemical physics), yes! ...

By inserting these rate constants into Kinetic master equations:

$$\boxed{\begin{aligned} \frac{dP_1(t)}{dt} &= -K_{2\leftarrow 1} P_1(t) + K_{1\leftarrow 2} P_2(t) \\ \frac{dP_2(t)}{dt} &= K_{2\leftarrow 1} P_1(t) - K_{1\leftarrow 2} P_2(t) \end{aligned}}$$

Proceeding empirically for now...

These kinetic Eqs. can be related to the G.R. analysis above if we associate

$$[4a] \qquad k_{2\leftarrow 1} = \Delta^2 \cdot 2\,\mathrm{Re} \int_0^\infty dt\ \mathrm{tr}_x \{ e^{-\beta h_1}\ e^{ih_1 t}\quad e^{-ih_2 t}\quad \} / Z_1 .$$

← ①→② thermal GR rate constant worked out above!

$$[4b] \qquad k_{1\leftarrow 2} = 2\,\mathrm{Re} \int_0^\infty dt\ \mathrm{tr}_x \{ e^{-\beta h_2}\ e^{ih_2 t}\quad e^{-ih_1 t}\quad \} / Z_2$$

← ②→① thermal GR rate const.

Consider master Eqs. [3] for $P_1(0)=1$, $P_2(0)=0$; and $t \cong 0$:

$$dP_1(t)/dt \cong -k_{2\leftarrow 1} = -\frac{dP_2(t)}{dt} \Rightarrow P_2(t) \cong k_{2\leftarrow 1} t \cong 1 - P_1(t)$$

Likewise: For $P_1(0)=0$, $P_2(0)=1$; and $t \cong 0$:

What about the long-time behavior

According to Eq. [3] $\quad \dfrac{P_1(\infty)}{P_2(\infty)} = \dfrac{k_{1\leftarrow 2}}{k_{2\leftarrow 1}}$

What do we expect on physical grounds:

exchange energy via non-adiabatic coupling ⇒ subsystems ①, ② are in thermal equilibrium.

Thus, we expect (hope!)

$$\boxed{\frac{Z_1}{Z_2} = \frac{P_1(\infty)}{P_2(\infty)}} = \frac{k_{1\leftarrow 2}}{k_{2\leftarrow 1}} \qquad [5]$$

In fact, the GR rate constants [4a,b] have this property!

To see why, consider the "frequency domain" version of [4a]: Note - this result holds for $\Delta = \Delta(\vec{x},\vec{p}) = \hat{\Delta}$ "detailed balance"

$$k_{2\leftarrow 1} = 2\pi \underset{\substack{\uparrow \\ \text{states of } \hat{h}_1}}{\sum_i} \frac{e^{-\beta E_1^{(i)}}}{Z_1} \underset{\substack{\uparrow \\ \text{states of } \hat{h}_2}}{\sum_f} \left|\langle \varphi_2^{(f)} | \hat{\Delta} | \varphi_1^{(i)} \rangle\right|^2 \delta(E_1^{(i)} - E_2^{(f)})$$

$$= 2\pi \sum_i \sum_f \frac{e^{-\beta E_2^{(f)}}}{Z_1} \left|\langle \varphi_2^{(f)} | \hat{\Delta} | \varphi_1^{(i)} \rangle\right|^2 \delta(E_1^{(i)} - E_2^{(f)}) \cdot \frac{1}{Z_2} \cdot Z_2$$

because of

$$= \frac{Z_2}{Z_1} \cdot k_{1\leftarrow 2}$$

agrees w/ [5]!

Hence, both long/short time behavior of the kinetic Eqs. Eqs. [3, 4] is correct, thus establishing strong plausibility of their validity.

Pause to consider explicit evaluation of GR rate constants for the Spin-Boson model.

The essential ingredient is the correlation function $C_1(t)$:

$$V_\alpha(\vec{x}) = \frac{1}{2}\sum_{k=1}^{N} \omega_k^2 \left(x_k - x_{k,\alpha}^{(0)}\right)^2 + V_\alpha^{(0)} \quad ; \alpha = 1,2$$

← the Spin-Boson model ⟺ linearly displaced harmonic oscillator diabatic potential surfaces

Since the eigenstates of both $\hat{h}_{1,2}$ factorize in these coordinates, so should all correlation corresponding to "equilibrium" preparation on surface 1 or 2.

Example: initial preparation in ground vibrational state of electronic state 1

Now:

$$C_1^{(\vec{0})}(t) = \Delta^2 \prod_{k=1}^{N} C_{1,k}^{(0)}(t) \cdot e^{-i\left(V_2^{(0)} - V_1^{(0)}\right)t}$$

(0) ← vibrational g.s.

Δ: nonadiabatic coupling strength factor out

1: surface 1

k: k^{th}

To be clear about meaning of $C_{1,k}^{(0)}(t)$:

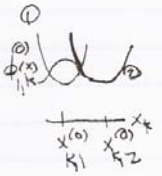


Fig. B

displaced harmonic oscillator

The generic DHO correlation fnctn. [Fig. B] can be evaluated as:

$$\boxed{C_{1,k}^{(0)}(t) = e^{b_k^2(e^{-i\omega_k t}-1)} \quad ; \quad b_k^2 = \frac{(x_{k,2}^{(0)}-x_{k,1}^{(0)})^2\omega_k}{2}\cdot\left[\frac{m}{\hbar}\right]}$$

The case of finite temperature preparation on, say, surface ① can also be evaluated:

$$C_{\beta,1}(t) = \Delta^2 e^{-i(V_2^{(0)}-V_1^{(0)})t}\prod_{k=1}^{N} C_{\beta,1}^{(k)}(t)$$

w/

$$\boxed{C_{\beta,1}^{(k)}(t) = e^{b_k^2(e^{-i\omega_k t}-1)+2\bar{n}_k(\cos\omega_k t-1)b_k^2} \quad ; \quad \bar{n}_k = [e^{\beta\overset{``\hbar"}{\downarrow}\omega_k}-1]^{-1}} \begin{array}{l} \nearrow 0 \text{ as } T\to 0 \\ \searrow \dfrac{kT}{\underset{\uparrow (\hbar)}{\omega_k}} \text{ as } T\to\infty \end{array}$$

// D.O.

One Displaced Oscillator vs Many:

Note: each 1D factor (for x_k) recurs perfectly with period $\frac{2\pi}{\omega_k}$

Thus, for a single coordinate system, GR analysis fails [correlation function does not decay irreversibly to 0].

But: for many D.O.'s with a range of (incommensurate) frequencies, dephasing of the recurrences in each mode occur → C(t) does decay irreversibly to zero.

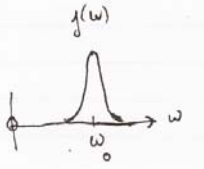
To see this, consider again the finite temp correlation fnctn:

$$C_{\beta,1}(t) = \Delta^2 e^{-i(V_2^{(0)}-V_1^{(0)})t}\underbrace{e^{\sum_{k=1}^{N}\{(e^{-i\omega_k t}-1)+2\bar{n}_k(\cos\omega_k t-1)\}b_k^2}}_{\bar{C}(t)}$$

It is possible to express this succinctly in terms of a spectral density function: $j(\omega) \equiv \sum_{k=1}^{N} b_k^2\,\delta(\omega-\omega_k)$

Consider, for example, $$j(\omega) = B^2 \underbrace{\frac{e^{-(\omega-\omega_0)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}}_{\to\ \delta(\omega-\omega_0)\ \text{as}\ \sigma\to 0}$$

for a continuous spectral density of



Assume $\omega_0 \gg \sigma$; Then: $$\bar{C}(t) = e^{\int_0^\infty d\omega\, j(\omega) \left\{ \left(e^{-i\omega t} - 1\right) + 2\bar{n}(\omega)\left[\cos\omega t - 1\right] \right\}}$$

$$\to \bar{n}(\omega) = \frac{1}{\left[e^{\beta\omega} - 1\right]}$$

$$\cong e^{B^2 \left\{ \underbrace{\left(e^{-i\omega_0 t} e^{-\sigma^2 t^2/2} - 1\right)}_{\text{exact}} + \underbrace{2\bar{n}(\omega_0)\left(\cos\omega_0 t\, e^{-\sigma^2 t^2/2} - 1\right)}_{\text{exact as } \sigma\to 0} \right\}}$$

$$\xrightarrow[t\to\infty]{} e^{-B^2\left[1 + 2\bar{n}(\omega_0)\right]} = \text{constant}$$

More generally, $$\bar{C}(t) \xrightarrow[t\to\infty]{} \underbrace{e^{-\int_0^\infty d\omega\, j(\omega)\left[2\bar{n}(\omega) + 1\right]}}_{\text{Debye–Waller factor}}$$

may or may not be precisely zero depending on details of $j(\omega)$; but for large B [vibronic = electron-phonon coupling] and/or large T], it should be very close to 0.

Strong electron-phonon limit: Gaussian Correlation functions

At short times:

$$\bar{C}(t) = e^{\int_0^\infty d\omega\, j(\omega) \left\{ \left(-i\omega t - \omega^2 t^2/2 + \cdots\right) + 2\bar{n}(\omega)\left[-\omega^2 t^2/2 + \cdots\right] \right\}}$$

$$\cong e^{-iAt - \Gamma t^2/2}$$

w:

$$A = \int_0^\infty d\omega\, j(\omega)\, \omega = \sum_{k=1}^N b_k^2 \omega_k \quad ; \quad \Gamma = \int_0^\infty d\omega\, \omega^2 \left[2\bar{n}(\omega) + 1\right] j(\omega) = \sum_{k=1}^N \omega_k^2 \left[2\bar{n}(\omega_k) + 1\right] b_k^2$$

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