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## The Spin-Boson Model, Part I.

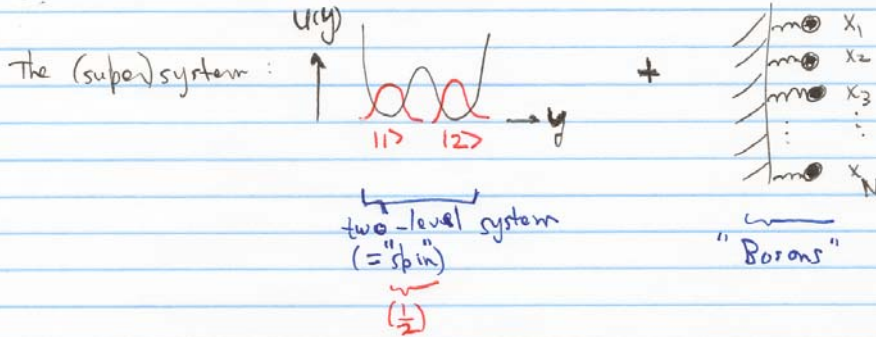
Topics covered:

- 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

① Aug 04,

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

Quantum Dynamics - Rob D. Coalson  
Univ. of Pittsburgh



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

$$\begin{aligned}
 H &= \begin{pmatrix} \epsilon & \Delta \\ \Delta & -\epsilon \end{pmatrix} + \sum_j \left( \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 x_j^2 \right) + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \sum_j \lambda_j x_j \\
 &= |1\rangle\langle 1| \left\{ \epsilon + \sum_j \left( \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 x_j^2 + \lambda_j x_j \right) \right\} + |2\rangle\langle 2| \left\{ -\epsilon + \sum_j \left( \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 x_j^2 - \lambda_j x_j \right) \right\} \\
 &\quad + \Delta (|1\rangle\langle 2| + |2\rangle\langle 1|) \\
 &= |1\rangle\langle 1| \left\{ \epsilon + \sum_j \left( \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left[ x_j + \frac{\lambda_j}{\omega_j^2} \right]^2 \right) \right\} + |2\rangle\langle 2| \left\{ -\epsilon + \sum_j \left( \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left[ x_j - \frac{\lambda_j}{\omega_j^2} \right]^2 \right) \right\} \\
 &\quad + \Delta (|1\rangle\langle 2| + |2\rangle\langle 1|) - \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}_{(|1\rangle\langle 1| + |2\rangle\langle 2|)} \sum_j \frac{\lambda_j^2}{2\omega_j^2} \leftarrow \text{invariant overall shift constant}
 \end{aligned}$$

②

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

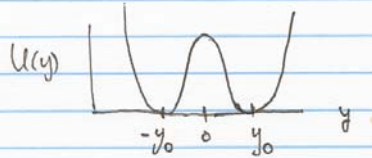
with (typically):  $\hat{\rho}_X(0) = e^{-\beta \hat{h}_1} / \text{tr}_X(e^{-\beta \hat{h}_1})$ ;  $\hat{h}_1 = \sum_j \left( \frac{\hat{p}_j^2}{2} + \frac{1}{2} \omega_j^2 [X_j + \lambda_j / \omega_j]^2 \right)$

Physical Underpinnings of the Spin-Boson model:

### (I) Multidimensional Tunneling

Consider (for simplicity) a tunneling coordinate,  $y$ , coupled to one <sup>harmonic</sup> oscillator coordinate,  $x$ .

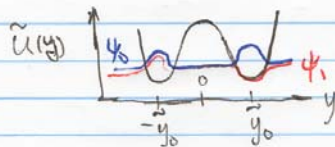
Let the "bare" tunneling potential:



Then, let:

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

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



Find (numerically) the eigenfunctions  $\psi_0, \psi_1$ , and energy the corresponding energy levels  $E_0, E_1$  of  $\tilde{U}$

③

Now exchange  $\Psi_{D,1}$  for Left and Right localized linear combinations

$$\Psi_L(y) = \frac{1}{\sqrt{2}} (\Psi_0(y) + \Psi_1(y)) ; \quad \Psi_R(y) = \frac{1}{\sqrt{2}} (-\Psi_0(y) + \Psi_1(y))$$

Next, take matrix elements of the (2-d) <sup>Hamiltonian</sup> subsystem in the  $|L\rangle, |R\rangle$  basis:

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

$\swarrow$   $\langle L|$        $\searrow$   $|R\rangle$

Note:

$$\langle R | h_y | R \rangle = \frac{1}{\sqrt{2}} (\langle \Psi_0 | + \langle \Psi_1 |) h_y (\Psi_0 + \Psi_1) \frac{1}{\sqrt{2}} = \frac{E_0 + E_1}{2} = \tilde{E}$$

Similarly:

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

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

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

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

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

$\leftarrow$  of (symmetric) Spin-Boson form  
SB

$$\cancel{\tilde{E}} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix}$$

irrelevant overall constant shift

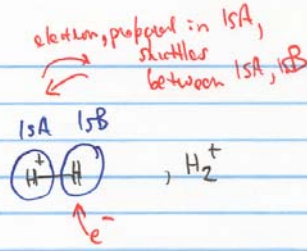
N.B.: extension to asymmetric SB case, and to multi-oscillator bath, is straightforward



(4)

(II) Electron-Phonon Coupling

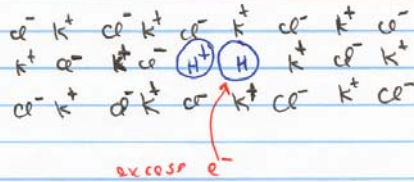
Consider 1<sup>st</sup> an isolated charge transfer system; e.g.:



or:



Now, embed this <sup>molecular 2-state</sup> 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.

$V_{int}(\vec{r}; \vec{x}_1, \dots, \vec{x}_N) = - \sum_{j=1}^N \frac{e_0 q_j}{|\vec{r} - \vec{x}_j|}$  ;  $e_0 = \text{proton charge}$  ;

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

tunneling electron ; lattice atoms

Letting:  $\vec{x}_j = \vec{x}_j^0 + \Delta \vec{x}_j$

$\Delta \vec{x}_j$  phonon displacement coordinate(s) for lattice ion  $j$ .

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

$V_{int}(\vec{r}; \vec{x}_1, \dots, \vec{x}_N) = V_{int}(\vec{r}; \vec{x}_j^0) + \sum_j \frac{\partial V_{int}}{\partial \vec{x}_j} \Big|_{\vec{x}_j^0} \cdot \Delta \vec{x}_j + \dots$

$\vec{x}_j^0 \equiv \vec{x}_j$

function of  $\vec{r}$  (only)

quadratic and higher order in phonon displacements

(5)

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

$$H = \frac{P_1^2}{2} + U_0(\vec{r}) + V_{int}(\vec{r}, \vec{x}_{0j}) + \sum_j f_j(\vec{r}) x_j + \sum_j \left( \frac{P_j^2}{2} + \frac{1}{2} \omega_j^2 x_j^2 \right)$$

↑ isolated  $H_2^+$  potential experiment 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  $|\tilde{S}_A(\vec{r})\rangle \rightarrow |L\rangle$  and

$|\tilde{S}_B(\vec{r})\rangle \rightarrow |R\rangle$  base states  
1-electron

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

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

↑ for  $H_2^+$  in  $sp^2$  (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  $f_j^{LR} \approx 0$  due to "exponentially small overlap between  $|\tilde{S}_A(\vec{r})\rangle$  and  $|\tilde{S}_B(\vec{r})\rangle$ " ["Condon approximation"]

Then (\*) is of Sp-invariant form (!)

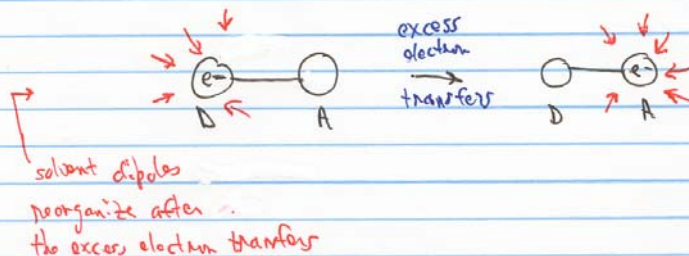
in this S.B. Hamiltonian are

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

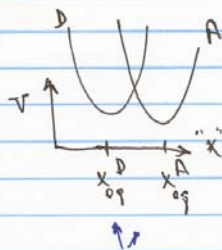
②

N.B.:

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



Thus the idea of:



is suggested

solvent hard: solvent 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-Boron model of electron transfer in a polar fluid is more subtle. [This is the subject of linear response theory and Marcus theory.]



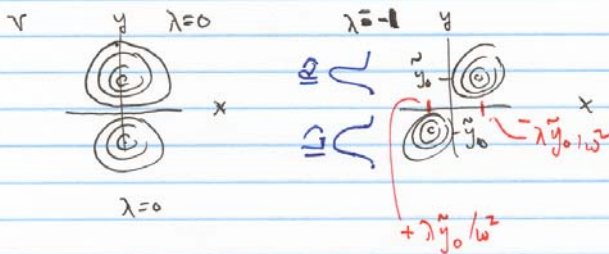
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Moving on to ...  
Dynamics under the Spin-Boson model.

First: 1) what are the appropriate initial conditions?

2) what properties do we want to calculate?

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



At  $t=0$ ,  
prepare in local equilibrium in the  $|L\rangle$  state.

At  $T=0$ ,  $\Psi_0(x, y) \cong \psi_L(y) \phi_0(x)$ , where  $\left[ \frac{p_x^2}{2} + \frac{1}{2} \omega^2 (x - \tilde{y}_0)^2 / \omega^2 \right] \phi_0(x) = \frac{\omega}{2} \phi_0(x)$

vibrational ground state  
↓

Thus the finite temperature analog is:

$$\hat{\rho}(0) = |L\rangle\langle L| e^{-\beta \hat{H}_L} / \text{tr}_x (e^{-\beta \hat{H}_L})$$

The main quantity of interest is:

$$\text{tr}_x \hat{\rho}(t) = \hat{\rho}_S(t) \leftarrow (2 \times 2) \text{ system reduced density matrix}$$

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



⑧

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

Consider the case that  $\Delta$  is small; use (Fermi) Golden Rule to evaluate short-time dynamics  
 $\uparrow$   
 barrier-tunnel matrix element

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

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

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

Again, the initial (super)system density matrix is:  $\hat{\rho}(0) = \frac{1}{\text{tr} \{ \exp(-\beta H) \}} \left[ \frac{1}{2} \langle 1| \langle 1| e^{-\beta h_1} + \frac{1}{2} \langle 2| \langle 2| e^{-\beta h_2} \right] \leftarrow Z_1$

Calculate the short-time evolution of the initial state  $|1\rangle|q_0\rangle$

$$\rho_1(t) = \langle q_0| \langle 1| e^{iH_{SB}t} |1\rangle \langle 1| e^{-iH_{SB}t} |1\rangle |q_0\rangle$$

↑ arbitrary  
optical wavepacket  
in  $\vec{x}$ -space

component of  $|q_0\rangle$  that remains on diabatic surface 1

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

Then:  $e^{-iH_{SB}t} = e^{-iH_0t} \left\{ 1 - i \int_0^t dt' V(t') - \int_0^t dt' \int_0^{t'} dt'' V(t') V(t'') + \dots \right\}$

with  $\hat{V}(t) = e^{iH_0t} (|1\rangle\langle 2| + |2\rangle\langle 1|) e^{-iH_0t} = \Delta \left( |1\rangle\langle 2| e^{i\omega_1 t} + |2\rangle\langle 1| e^{-i\omega_1 t} \right)$

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Now:  $\langle 1 | e^{-iH_S B t} | 1 \rangle = e^{-i h t} \left( 1 - \int_0^t \int_0^{t'} \langle 1 | V(t) V(t') | 1 \rangle + \dots \right)$  ↗  $G(\Delta^4)$

$$\Delta \left( \int_0^t \int_0^{t'} e^{i h t'} e^{-i h_2 t'} + \int_0^t \int_0^{t'} e^{i h_2 t'} e^{-i h t'} \right)$$

$$\Delta \left( \int_0^t \int_0^{t'} e^{i h t''} e^{-i h_2 t''} + \int_0^t \int_0^{t'} e^{i h_2 t''} e^{-i h t''} \right)$$

or:

$$\langle 1 | e^{-iH_S B t} | 1 \rangle = e^{-i h t} \left( 1 - \Delta^2 \int_0^t \int_0^{t'} e^{i h t'} e^{-i h_2 t'} e^{i h_2 t''} e^{-i h t''} + \dots \right)$$

$$e^{-i h_2 (t' - t'')}$$

Thus:

$$P_f(t) \approx \langle \varphi_0 | \left( 1 - \Delta^2 \int_0^t \int_0^{t'} e^{i h t''} e^{i h_2 (t' - t'')} e^{-i h t'} \right) e^{-i h t} | \varphi_0 \rangle$$

$$= 1 - \Delta^2 \cdot 2 \text{Re} \int_0^t \int_0^{t'} \langle \varphi_0 | e^{i h t''} e^{-i h_2 (t' - t'')} e^{-i h t'} | \varphi_0 \rangle$$

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

Now:

$$P_f(t) = 1 - \Delta^2 \cdot 2 \text{Re} \int_0^t \int_0^{t'} G(t' - t'') ; \quad G(t) = e^{i \epsilon_p^{(j)} t} \langle \varphi_p^{(j)} | e^{-i h_2 t} | \varphi_p^{(j)} \rangle$$

Finally, consider the finite temperature analog:

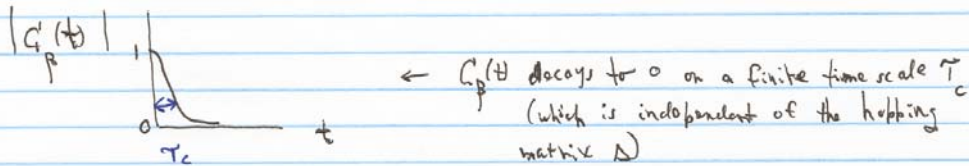
$$P_f(t) = \text{tr}_x \langle 1 | \hat{\rho}(t) | 1 \rangle = \int d\vec{x} \langle 1 | e^{-iH_S B t} | 1 \rangle \langle \varphi_p^{(j)} | \varphi_p^{(j)} \rangle e^{-\beta \epsilon_p^{(j)}} e^{i H_S B t}$$

$$\approx 1 - \Delta^2 \cdot 2 \text{Re} \int_0^t \int_0^{t'} G_\beta(t' - t'')$$

(10)

$$w \quad G_p^i(t) = \frac{\sum_j \beta \epsilon_1^{ij} G^j(t)}{Z_1} = \frac{1}{Z_1} \left\{ \begin{array}{cc} i h_1 \tau & -i h_2 \tau \\ \beta_1 e & e \end{array} \right\} ; \frac{\beta}{\beta_1} = \frac{\psi h_1}{Z_1}$$

It can be shown, by direct evaluation of  $G_p^i(t)$  for  $h_{1,2}$  corresponding to the Spin Bore model, that in many cases (particularly when the electron-phonon coupling is large);



If so, then for small  $\Delta$ :

$$\Delta^2 \cdot 2 \operatorname{Re} \int_0^t dt' G_p^i(t-t') \stackrel{t' \gg \tau_c}{=} \Delta^2 \cdot 2 \operatorname{Re} \int_0^\infty du G_p^i(u) = \Delta^2 \int_{-\infty}^\infty du G_p^i(u) \equiv K \quad z \ll 1$$

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

Is this info useful for computing long-time dynamics of the SB model?

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

By inserting these rate constants into kinetic master equations:

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

(11)

Proceeding empirically for now...

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

$$[4a] \quad k_{2 \leftarrow 1} = \frac{2}{\Delta} \operatorname{Re} \int_0^{\infty} dt \operatorname{tr}_x \left\{ e^{-\beta H_1} e^{i H_1 t} e^{-i H_2 t} \right\} / Z_1 \quad \leftarrow \textcircled{1} \rightarrow \textcircled{2} \text{ thermal GR rate constant worked out above!}$$

$$[4b] \quad k_{1 \leftarrow 2} = 2 \operatorname{Re} \int_0^{\infty} dt \operatorname{tr}_x \left\{ e^{-\beta H_2} e^{i H_2 t} e^{-i H_1 t} \right\} / Z_2 \quad \leftarrow \textcircled{2} \rightarrow \textcircled{1} \text{ thermal GR rate const.}$$

Consider matrix Eq. [3] for  $P_1(0)=1, P_2(0)=0$ ; and  $t \approx 0$ :

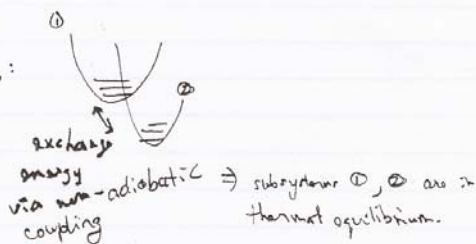
$$dP_1(t)/dt \approx -k_{2 \leftarrow 1} = -\frac{dP_2(t)}{dt} \Rightarrow P_2(t) \approx k_{2 \leftarrow 1} t \approx 1 - P_1(t)$$

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

What about the long-time behavior

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

What do we expect on physical grounds:



This, we expect (hope!)

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

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



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

$$\begin{aligned}
 k_{2 \leftarrow 1} &= 2\pi \sum_i \frac{e^{-\beta E_1^{(i)}}}{Z_1} \sum_f \frac{1}{f} |\langle \psi_2^{(f)} | \hat{\Delta} | \psi_1^{(i)} \rangle|^2 \delta(E_1^{(i)} - E_2^{(f)}) \\
 &= 2\pi \sum_f \frac{1}{f} \sum_i \frac{e^{-\beta E_2^{(f)}}}{Z_2} |\langle \psi_2^{(f)} | \hat{\Delta} | \psi_1^{(i)} \rangle|^2 \delta(E_1^{(i)} - E_2^{(f)}) \cdot \frac{1}{Z_1} Z_2 \\
 &= \frac{Z_2}{Z_1} \cdot k_{1 \rightarrow 2} \quad \leftarrow \text{because of } \dots \text{ agrees w/ [5]!}
 \end{aligned}$$

Hence, both long/short time behavior of <sup>the kinetic eqs.</sup> 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  $C(t)$ :

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

← 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:  $C_{11}^{(10)}(t) = \frac{1}{N} \sum_{k=1}^N \Delta_k$

nonadiabatic coupling strength factor out

$\Delta_k = \langle \phi_1^{(0)} | \phi_2^{(0)} \rangle e^{-i(\omega_k^{(2)} - \omega_k^{(1)})t}$

← vibrational g.s. ←  $\phi_1^{(0)}$   
←  $\phi_2^{(0)}$   
← surface 1

Things to check about meaning of  $C_{11}^{(10)}(t)$ :

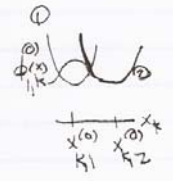


Fig. B

(14)

The generic displaced harmonic oscillator correlation fnctn. [Fig. B] can be evaluated as:

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

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

$$C_{\beta,1}^{(k)}(t) = e^{-\frac{1}{2} (r_2^{(0)} - r_1^{(0)})^2} \prod_{k=1}^N C_{\beta,1}^{(k)}(t)$$

$$C_{\beta,1}^{(k)}(t) = e^{-\frac{1}{2} b_k^2 (e^{-i\omega_k t} - 1) + 2\bar{n}_k (\cos \omega_k t - 1) b_k^2} ; \bar{n}_k = \left[ \frac{1}{e^{\beta \hbar \omega_k} - 1} \right]^{-1}$$

$\rightarrow 0$  as  $T \rightarrow 0$   
 $\rightarrow \frac{\hbar T}{\hbar \omega_k}$  as  $T \rightarrow \infty$   
 $\left( \frac{\hbar}{k} \right)$

D.O.  
One Displaced Oscillator or Many:

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

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

But: for many D.O.'s with a range of (incommensurate) frequencies, dephasing of the resonances in each mode occurs  $\rightarrow C(t)$  does decay inevitably to zero.

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

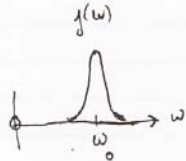
$$C_{\beta,1}^{(A)}(t) = e^{-\frac{1}{2} (r_2^{(0)} - r_1^{(0)})^2} \prod_{k=1}^N \left\{ e^{-\frac{1}{2} b_k^2 (e^{-i\omega_k t} - 1) + 2\bar{n}_k (\cos \omega_k t - 1) b_k^2} \right\} b_k^2$$

$\underbrace{\hspace{10em}}_{\bar{C}(t)}$

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

(15)

Consider, for example,  $f(\omega) = B^2 \frac{e^{-(\omega-\omega_0)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}$  for a continuous spectral density of  $\rightarrow \delta(\omega-\omega_0)$  as  $\sigma \rightarrow 0$



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

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

exact as  $\sigma \rightarrow 0$

$$\rightarrow e^{-B^2 [1 + 2\bar{n}(\omega_0)]} = \text{constant}$$

More generally,  $\bar{C}(t) \rightarrow e^{-\int_0^\infty d\omega j(\omega) [2\bar{n}(\omega) + 1]}$   
 ↳ Dobys-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:

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

$$\approx e^{-iAt - Pt^2/2}$$

w:

$$A = \int_0^\infty d\omega j(\omega) \omega = \sum_{k=1}^N \frac{2}{\hbar \kappa \omega_k} ; \quad P = \int_0^\infty d\omega \omega^2 [2\bar{n}(\omega) + 1] j(\omega) = \sum_{k=1}^N \omega_k^2 [2\bar{n}(\omega_k) + 1] \frac{2}{\hbar \kappa}$$



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