Klaus's work on the Spin-Boson Problem*

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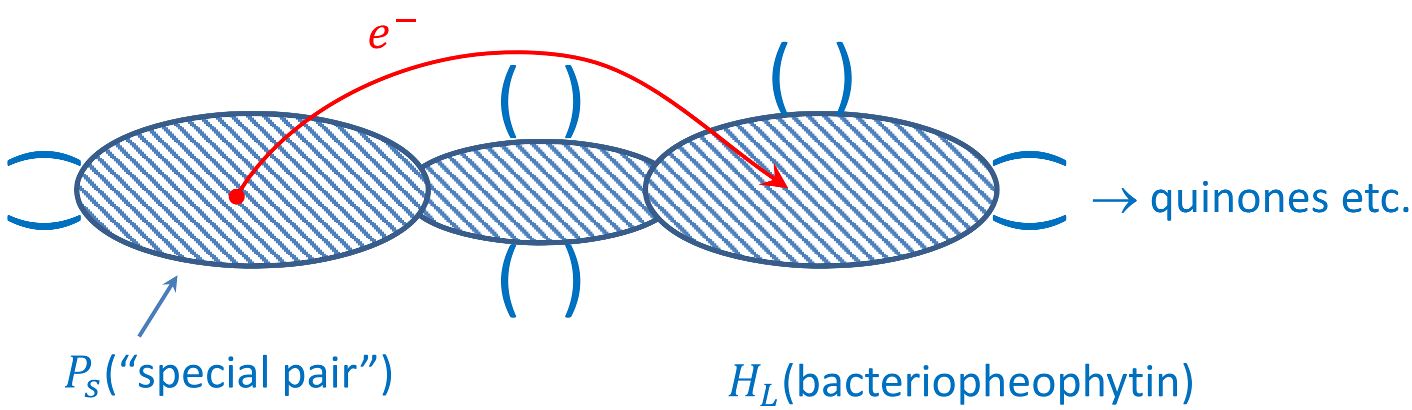
*K. Schulten and M. Tesch, Chemical Physics **158**, 421 (1991)
Dong Xu and K. Schulten, Chemical Physics **182**, 91 (1994) ("XS")

Electron transfer ($P_S H_L \to P_S^+ H_L^-$) in photosynthetic reaction center of Rhodopseudomonas Viridis

a naïve condensed-matter physicist's cartoon:



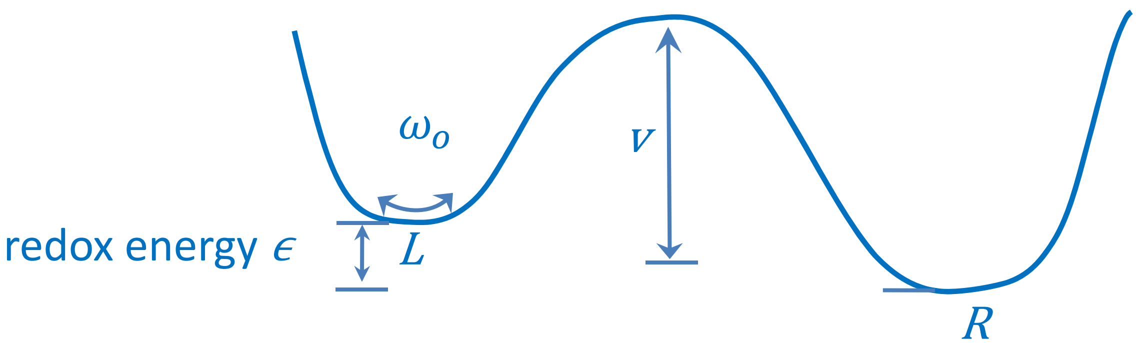
Experimental fact: backward rate at $RT \sim 10\text{ns}^{-1}$
forward rate at $RT \sim 3\text{ps}^{-1}$

$\downarrow$

increases by factor ~4 by 8K

Suggests: QM effects important
also: little dependence on redox energy

From QM point of view, special case of more general 2–state problem



In present case, "environment" is vibrating nuclei of protein: nuclear coordinates coupled to tunnelling electron by Coulomb force.

In general case need to consider

(a) effect of coupling to environment on barrier transmission

(b) effect of coupling to environment on coherence between $|L\rangle$ and $|R\rangle$.

but in present case Born-Oppenheimer approximation probably good,

$\Rightarrow$ can neglect effect (a) $\Rightarrow$ spin-boson model

Generic spin-boson model:

$$\hat{H} = \hat{H}_{\text{sys}} + \hat{H}_{\text{env}} + \hat{H}_{\text{coup}}$$

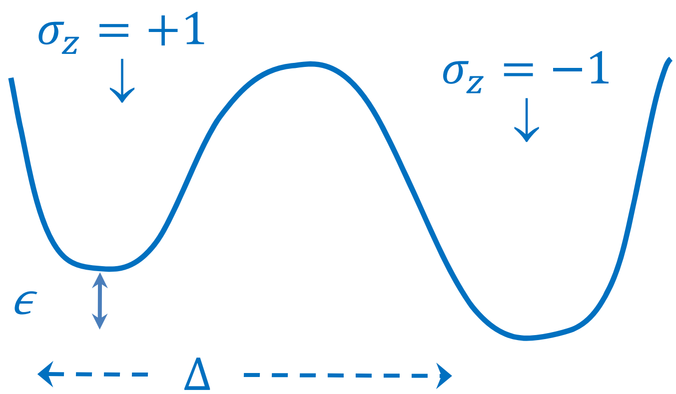
↑ system ↑ environment ↑ coupling

$$\hat{H}_{\text{sys}} = \frac{1}{2}\Delta\hat{\sigma}_x + \frac{1}{2}\epsilon\hat{\sigma}_z$$

← "spin"

↑ "bare" tunneling matrix element

↑ offset

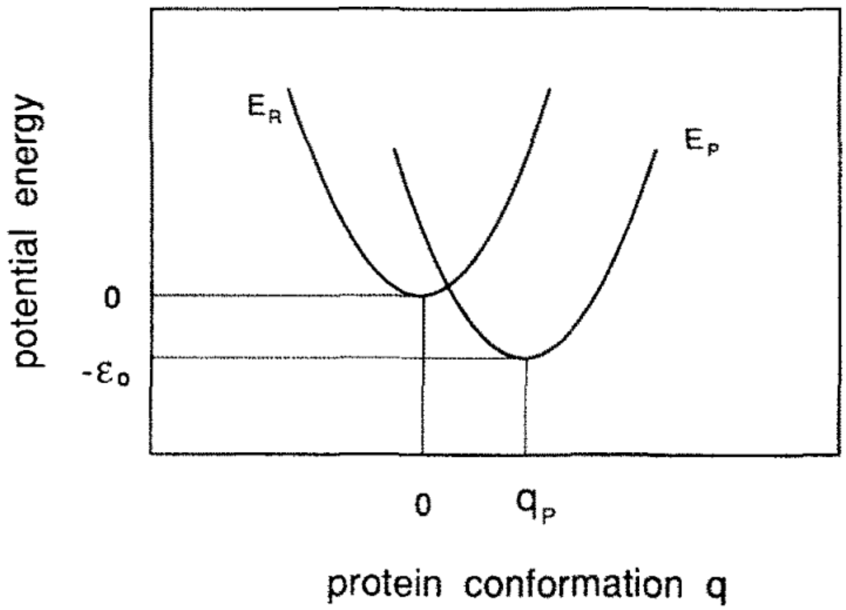


$$\hat{H}_{\text{env}} = \sum_{\alpha=1}^{N}\left(\hat{p}_\alpha^2/2m_\alpha + \frac{1}{2}m_\alpha\omega_\alpha^2\hat{x}_\alpha^2\right)$$

← "bosons" (SHO's)

$$\hat{H}_{\text{coup}} = \frac{1}{2}\hat{\sigma}_z\sum_{\alpha=1}^{N} c_\alpha\,\hat{x}_\alpha$$

In our case, multimode Marcus model:



Correspondence:

tunneling electron $\rightarrow$ spin

bare tunneling amplitude $\rightarrow \Delta$

nuclear coordinates $\rightarrow x_\alpha \equiv q_\alpha - \frac{1}{2} q_{o\alpha}$

coupling constant $\rightarrow c_\alpha \equiv m_\alpha \omega_{o\alpha}^2 q_{o\alpha}$

redox energy $\rightarrow \epsilon$

We would like to know transfer rate $k(\epsilon, T)$ as function of redox energy ϵ and temperature T.

Crucial feature of spin-boson problem:

Provided we are interested only in dynamics of spin, complete information about effect of environment is encapsulated in

$$J(\omega) \equiv \frac{\pi}{2} \sum_{\alpha=1}^{N} \frac{c_\alpha^2}{m_\alpha \omega_\alpha} \delta(\omega - \omega_\alpha)$$

← coupling spectral density

which can often be obtained from classical arguments (e.g. in superconducting devices, from experiment in classical regime). Schulten et al. obtain from classical MD simulation:

$$J(\omega) = \frac{\alpha\omega}{1 + \omega^2\tau^2}$$

(on α:) dimensionless (XS:η)

For $\omega\tau \ll 1$, dissipation is ohmic with $\alpha \gg 1$, i.e. strongly overdamped.

Some estimated numbers for RPV (in secs)

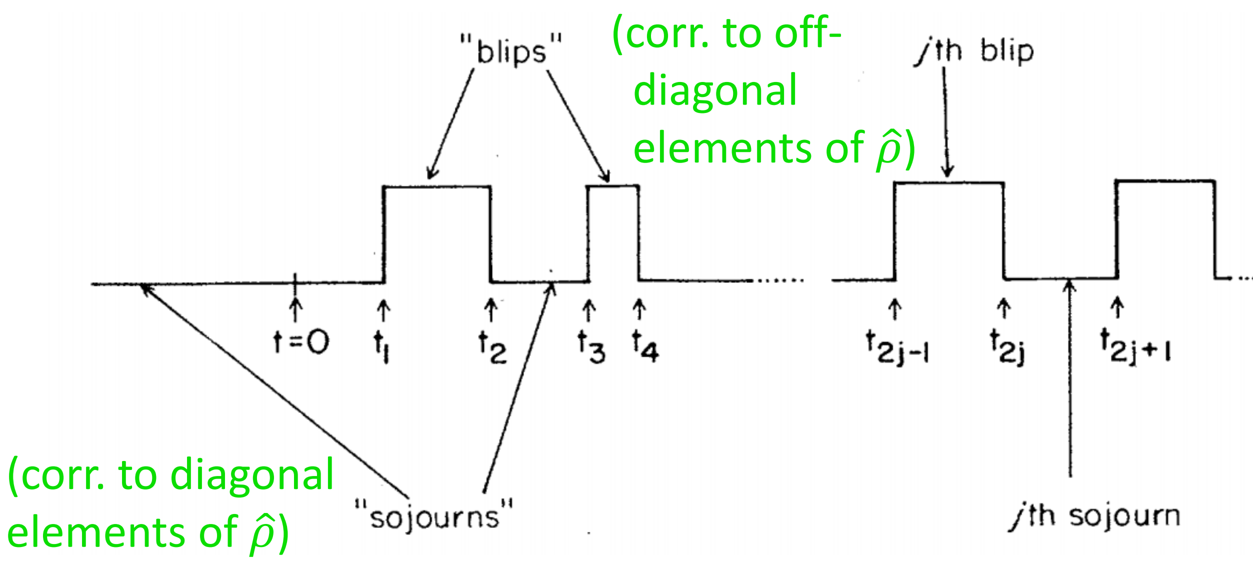
$\hbar/kT$	$\sim 25\ f\mathrm{sec}$
τ (from simulation)	$\sim 100\ f\mathrm{sec}$
$\hbar/\sigma$ (from simulation) ↑ (σ:) en. fluctuation	$\sim 3\ f\mathrm{sec}$
hence $\alpha = \sigma^2\tau/hkT$	~ 25
$\Delta^{-1}(RT)$	$\sim 100\ f\mathrm{sec}$
$\Longrightarrow (\Delta^2\tau)^{-1}$	$\sim 100\ f\mathrm{sec}$
forward transfer rate $k_{\mathrm{exp}}^{-1}(RT)$	~ 10 psec

so k_{exp} slowest rate in problem, but $\Delta \sim \tau^{-1} \sim$ cutoff for "ohmic" behavior however, $k_{\mathrm{exp}} \ll \tau^{-1}$

General treatment of spin-boson problem*

Formulation of problem: Given form of $J(\omega)$ (and Δ, ϵ, T), set initial condition $\sigma_z(t) = +1$. Evolve according to $\hat{H}_{tot}$, calculate $\langle\hat{\sigma}_z(t)\rangle \equiv P(t)$, (and hence, if it is exponentially decaying, transfer rate $k \equiv -lnP(t)/t$).

Step 1 (general). Derive exact formal expression for $P(t)$ in terms of $J(\omega), \Delta, \epsilon$ and T, and represent in graphical form



Step 2. Under certain conditions, justify “noninteracting blip approximation” (NIBA), convert to much simpler form (in principle soluble by Laplace transform, if one can do the integrals)

Step 3. Obtain analytic expression for $P(t)$ and thus when appropriate for $k(\epsilon, T)$.

*A.J. Leggett, S. Chakravarty, A.T. Dorsey, Matthew P.A. Fisher, A. Garg, and W. Zwerger. Revs. Mod. Phys. 59, 1 (1987).

In the overdamped case (only) step 2 gives the "golden-rule" result

$$P(t) = P(\infty) + \big(1 - P(\infty)\big)\exp - \Gamma t$$

$$P(\infty) \equiv -tanh(\epsilon/k_B T)$$

$$\Gamma(\Delta, \epsilon, T) = \left(\frac{\Delta}{\hbar}\right)^2 \int_0^\infty dt\ \cos(\epsilon t/\hbar) cos(Q_1(t)/\pi\hbar)\exp - Q_2(t)/\pi\hbar$$

where

$$Q_1(t) \equiv \int_0^\infty \frac{d\omega}{\omega^2} J(\omega) \sin \omega t$$

$$Q_2(t) \equiv \int_0^\infty \frac{d\omega}{\omega^2} J(\omega)(1 - \cos \omega t) \coth \beta\hbar\omega/2$$

In the limit $\tau \rightarrow \infty$ (pure ohmic dissipation with cut off $\omega_c \gg \Delta, \epsilon, k_B T$) $\Gamma(\Delta, \epsilon, T)\big(\equiv k(\epsilon, T)\big)$ can be evaluated analytically:

$$k(\epsilon, T) = \left(\frac{\Delta^2}{\omega_c}\right) f(\epsilon, T)$$

where

for $\epsilon = 0, T \neq 0$ $\quad f(T) = \text{const.} (k_B T/\hbar\omega_c)^{2\alpha - 1}$

for $T = 0, \epsilon \neq 0$ $\quad f(\epsilon) = \text{const.} (\epsilon/\hbar\omega_c)^{2\alpha - 1}$

for T, ϵ both $\neq 0$ messy formula involving Euler Γ-function

However, for the RPV tunneling problem the cut off frequency $\omega_c \sim \tau^{-1}$ is quite comparable to Δ, ϵ, T, so we must keep the full form of $J(\omega)$, namely

$$J(\omega) = \frac{\alpha\omega}{1 + \omega^2\tau^2}$$

XS show that for $k_B T \gg \hbar/\tau$ the resulting expression for Γ, hence for $k(\epsilon, T)$ can be evaluated analytically and the result expressed in the Marcus-like form (Garg et al., 1985)

$$k(\epsilon, T) = \text{const.}\frac{1}{\delta}\exp -(\epsilon - \epsilon_m)^2/2\delta^2$$

where

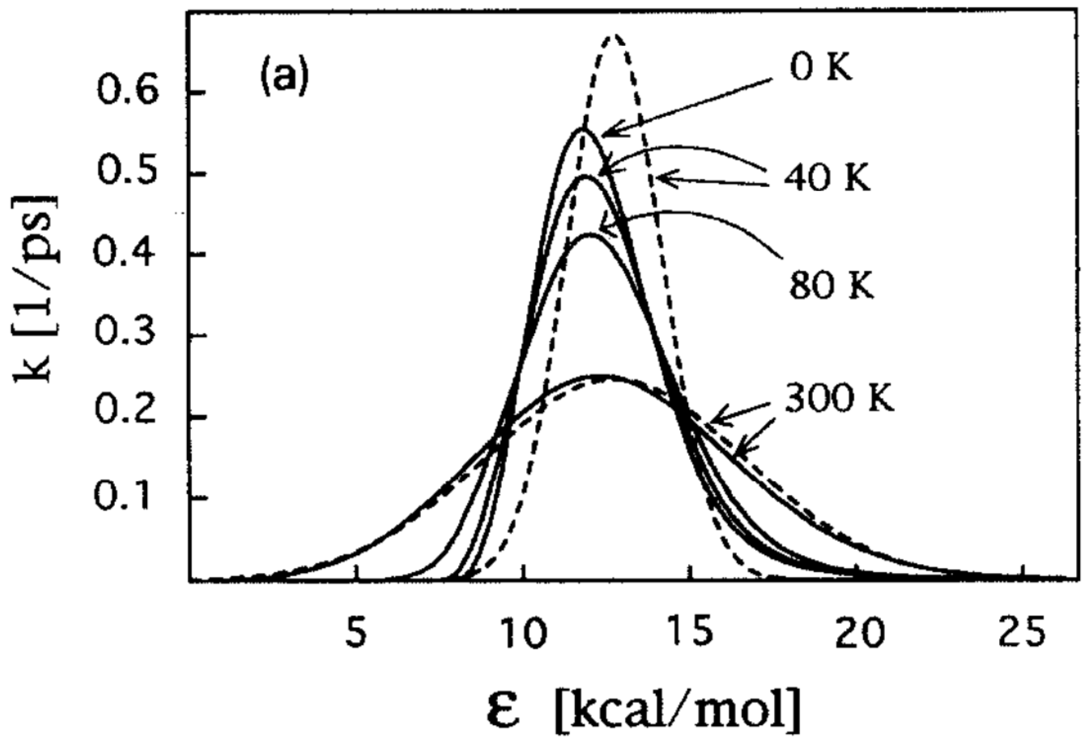
$\epsilon \equiv$ c-number well bias ($\equiv$ redox energy)

$$\epsilon_m \equiv \frac{}{\pi}\int_0^\infty \frac{J(\omega)}{\omega} \quad d\omega \ (\equiv \text{solvation energy})$$

$$\delta^2 \equiv \frac{\hbar}{\pi}\int_0^\infty J(\omega) \coth(\beta\hbar\omega/2) d\omega \ (\equiv \Delta\epsilon^2, \text{fluctuation energy})$$

quantum fluctuations

At lower T it is necessary to calculate $k(\epsilon, T)$ numerically, inputting the specific values of α and τ for RPV. XS's results:



Conclusions:

(1) At RT, simple Marcus theory works well (not too surprising, since $kT_R > \hbar/\tau$)
(2) At lower T (but not $T = 0$), generalized Marcus theory with $TF \rightarrow QF$ works well
(3) At $T{\sim}0$, (or for more general problems, e.g. liquid solvation) need to evaluate GR expression numerically.

↑ Golden Rule

(would "boson sampling" help?)