* Marcus theory
* Primary electron transfer in the photosynthetic reaction center form purple bacteria
* Quantum theory for the inverted regime -- the exponential energy-gap law

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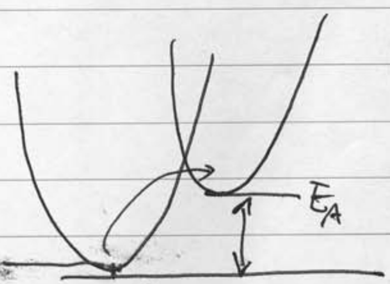
Marcus theory.

Use a spin-boson Hamiltonian to describe electron transfer in condensed phase.

$$DA \longrightarrow D^+A^-$$

$$H = \begin{bmatrix} \varepsilon_D + \hat{h}_D & J \\ J & \varepsilon_A + \hat{h}_A \end{bmatrix}$$



$$\hat{h}_D = \sum_\alpha \left\{ \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 x_\alpha^2 \right\}$$

$$\hat{h}_A = \sum_\alpha \left\{ \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 (x_\alpha - d_\alpha)^2 \right\}$$

$$= \hat{h}_D + \lambda - \sum_\alpha m_\alpha \omega_\alpha^2 d_\alpha x_\alpha$$

$$\lambda = \sum_\alpha \lambda_\alpha = \sum_\alpha \frac{1}{2} m_\alpha \omega_\alpha^2 d_\alpha^2$$

← displaced.

$$\therefore\ H = \begin{bmatrix} \varepsilon_D + \hat{h}_D & 0 \\ 0 & \varepsilon_A + \hat{h}_A \end{bmatrix} + \begin{bmatrix} 0 & J \\ J & 0 \end{bmatrix}$$

$$= H_0 + V$$

Initial condition $\rho_{init} = |D\rangle\langle D| \otimes \sigma^{eq}_{\hat{h}_A}$.

Applying Fermi's Golden Rule.

$$k_{A\leftarrow D} = \frac{|J|^2}{\hbar^2} \cdot \int_{-\infty}^{\infty} dt \cdot e^{\frac{i}{\hbar}(\varepsilon_D - \varepsilon_A)t} \cdot \left\langle e^{\frac{i}{\hbar}\hat{h}_D t}\, e^{-\frac{i}{\hbar}\hat{h}_A t} \right\rangle_{\hat{h}_D}$$

Assume the vibrational Hamiltonians $\hat{h}_D$ & $\hat{h}_A$ are classical $\Rightarrow$

In the classical limit.

$$\left\langle e^{\frac{i}{\hbar}\hat{h}_D t}\, e^{-\frac{i}{\hbar}\hat{h}_A t} \right\rangle_{\hat{h}_D} = \left\langle e^{\frac{i}{\hbar}(\hat{h}_D - \hat{h}_A)t} \right\rangle_{\hat{h}_D}$$

$$= \prod_\alpha e^{-\frac{i}{\hbar}\lambda_\alpha t} \cdot e^{-\frac{1}{\hbar^2}\lambda_\alpha \cdot k_B T \cdot t^2}$$

$$= e^{-\frac{i}{\hbar}\lambda t} \cdot e^{-\frac{1}{\hbar}\cdot \lambda \cdot k_B T \cdot t^2}$$

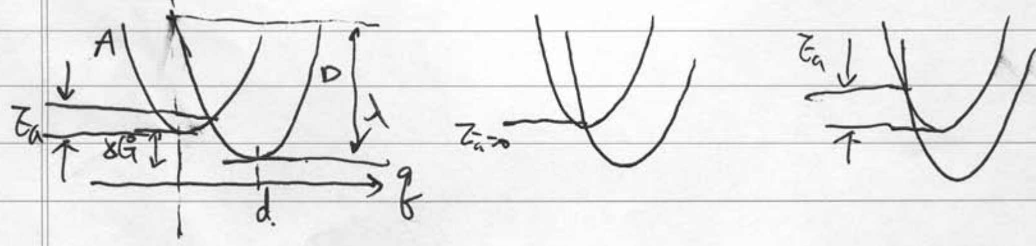
timeless

i, Marcus theory predicts the ΔG°

$$k_{A\leftarrow D} = \frac{|J|^2}{\hbar^2}\cdot\hbar\cdot\sqrt{\frac{\pi}{\lambda k_B T}}\cdot e^{-\frac{(\varepsilon_A-\varepsilon_D+\lambda)^2}{4\lambda k_B T}}$$

follows Arrhenius thermal activation form.
define Marcus parabolas via a collective coordinate.
$\Delta G^\circ = \varepsilon_A - \varepsilon_D$. ← driving force.

$\Delta G^\circ > -\lambda$ | $\Delta G^\circ = -\lambda$ | $\Delta G^\circ < -\lambda$



$\Delta G^\circ \downarrow$, $k\uparrow$ | maximal k | $\Delta G^\circ\downarrow$, $k\downarrow$

normal regime | optimal k, activationless ε_T | inverted regime.

⇒ example in detail see P.14 of Lecture 30 here.

This is most frequently discussed via the Marcus plot.

also called driving force

$$\ln k \approx \ln k_0 - \frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}$$. as a function of $-\Delta G^\circ$

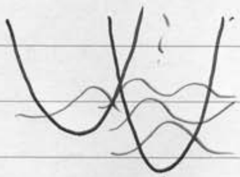
minus sign

Note : ① optimal ΔG° occurs @ $-\lambda$, when $\lambda \uparrow$, then optimal $\Delta G^\circ_{opt} \downarrow$ (more negative)

② at small ΔG°, $\lambda \uparrow$, rate $\downarrow$ $\Rightarrow$ trapping —

③ discrepancies in the inverted regime is due to tunneling contribution.

normal regime



Small vib. tunneling overlap, tunneling not important

large vib. overlap (Frank-Condon factor). tunneling pronounced.

④ valid at small J

~~usually~~ J depends on orbital overlap, usually decays exponentially. $J \approx J_0 \cdot e^{-\frac{\beta(R-R_0)}{2}}$

β : 0.8 − 1.2 $\mathring{A}^{-1}$

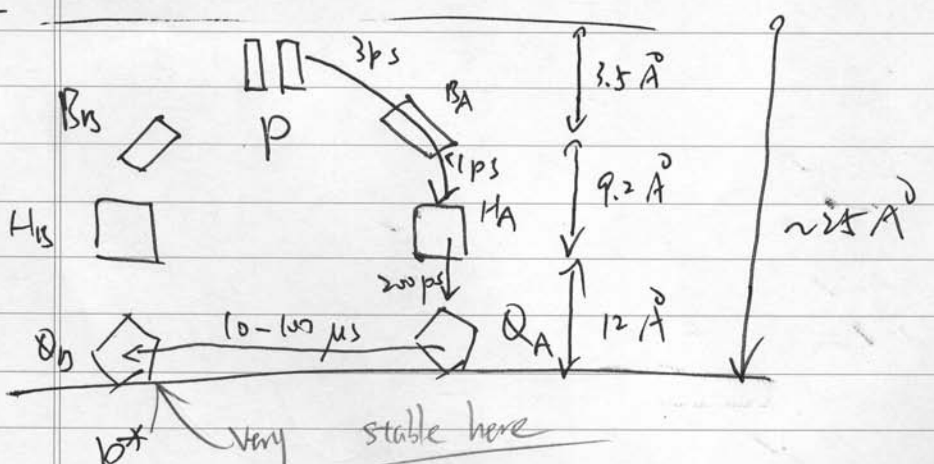
Photosynthetic ET

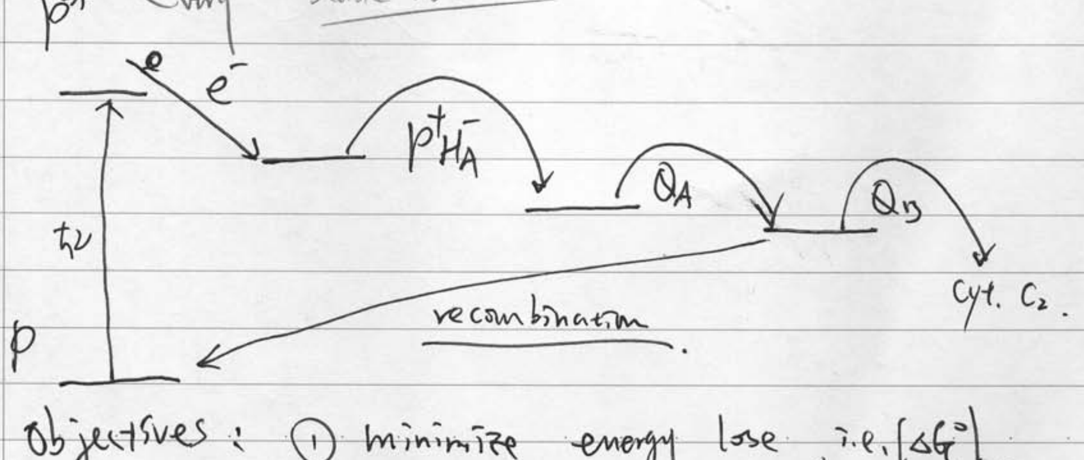
A very beautiful application of Marcus theory is photosynthetic electron transfer in reaction centers of photosynthetic systems;

* highly conserved arch. in biology.

from bacteria to higher plants, almost no change.

membrane





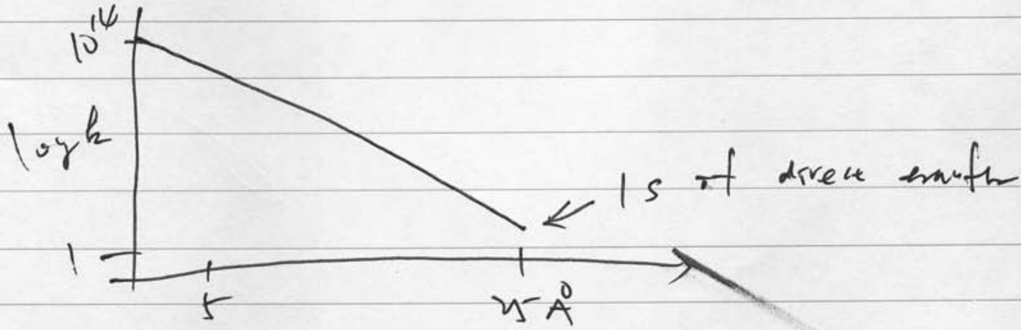
Objectives: ① minimize energy lose, i.e. $|\Delta G^0|$.
② minimize back transfer rate, recombination.

Design principles: How nature achieve this ??

1. put multiple states in there to get exponential speed up.

   ⇒ in order to move $\bar{e}$ across 25 Å

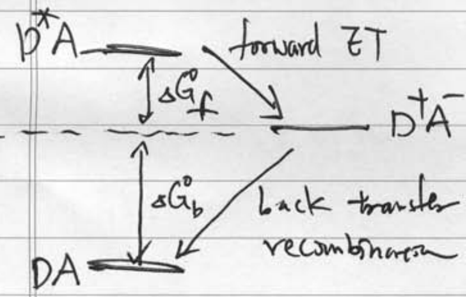
   (a) if direct transfer (Chl – Chl)



2. Utilized optimal rate, $\Delta G^0 \simeq -\lambda_s$
3. polar medium represents large λ_s and thus need large negative ΔG^0 to achieve ~~effective~~ efficient transfer ⇒ would be a problem.

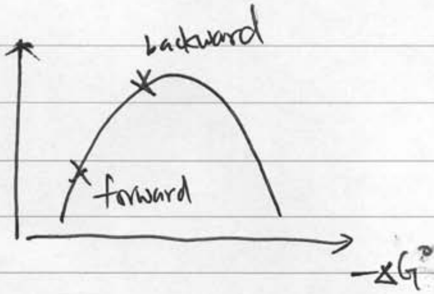
   ⇒ use protein hydrophobic enclosure to achieve small λ_s.

effects of less polar protein environment.



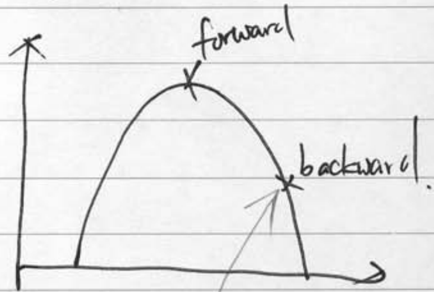
$$-\Delta G^0_b > -\Delta G^0_f$$

large λ_s



No good.

small λ_s



good. Small λ_s makes back transfer inverted

small λ_s also reduce energy lose for achieving optimal rate.

So, run photosynthesis in butter, not water!!

④ ~~Qa~~ stablize $\bar{e}$ on Q_B ⇒ use polar residue around Q_B

ie is apprant from crystal structure, also molecular simulation studies show that the reorganization energies at Q_A & Q_B and are sig. difference

estimate:

$\lambda_{Q_A} \approx 0.6 - 0.9$ eV

$\lambda_{Q_B} \approx 1.23$ eV

traps the charge

$\boxed{\text{⑤ put a cap on !! there is a big H subunit of the protein .}}$

Thus, natural photosynthetic reaction centors represent highly optimized ET ~~engine~~ device to achieve highly efficient & specific electron transfer ⇒ Natural knows / studies Marcus theory ∴, no wonder after 4B years of ~~ago~~ time.

The discrepancy in the inverted regime is due to quantum tunneling effects, to correctly describe this, we need a quantal theory for ET ⇒ we have already done TC, just evaluate the "dephasing function" quantum mechanically :

$$F(t) = \left\langle e^{\frac{i}{\hbar}\hat{h}_D t} e^{-\frac{i}{\hbar}\hat{h}_A t} \right\rangle_{\hat{h}_D} = \prod_\alpha \left\langle e^{-\frac{i}{\hbar} d_\alpha \hat{p}_\alpha(t)} e^{\frac{i}{\hbar} d_\alpha \hat{p}_\alpha(0)} \right\rangle$$

$$= \prod_\alpha e^{+D_\alpha\left[(\bar{n}_\alpha+1)(e^{-i\omega_\alpha t}-1) + \bar{n}_\alpha\cdot(e^{i\omega_\alpha t}-1)\right]}$$

with $D_\alpha = \frac{m\omega_\alpha d_\alpha^2}{2\hbar}$

note $\lambda_\alpha = \hbar \cdot D_\alpha \cdot \omega_\alpha$.

Note that at low-T, $\bar{n}_\alpha \approx 0$, the expression predicts a temperature-independent rate ⇒ quantum tunneling effects dominate the low-T ET., different from classical Marcus theory.

for low frequency mode or high temperature,

$$2\bar{n}_\alpha + 1 = \coth\left(\frac{\beta\hbar\omega_\alpha}{2}\right) \approx \frac{2}{\beta\hbar\omega_\alpha} = \frac{2}{\hbar\omega_\alpha} \cdot k_B T \text{, then}$$

one can recover the Marcus theory,

for high frequency mode or low T, ~~where~~ we

consider $\bar{n}_\alpha \approx 0$ & $\hbar\omega_\alpha \gg k_B T$.

then we should get the tunneling effect.

⇒ focus on a single mode.

$$F_\alpha(t) \approx e^{-D_\alpha} \cdot e^{+D_\alpha \cdot e^{-i\omega_\alpha t}}$$

rate $k_{A\leftarrow D} = \frac{|J|^2}{\hbar^2} \cdot \int_{-\infty}^{\infty} dt \cdot e^{\frac{i}{\hbar}(\varepsilon_D - \varepsilon_A)t} \cdot e^{-D_\alpha} \cdot e^{+D_\alpha \cdot e^{-i\omega_\alpha t}}$

$$= \frac{|J|^2}{\hbar^2} \cdot e^{-D_\alpha} \cdot \int_{-\infty}^{\infty} dt \cdot e^{\frac{i}{\hbar}(\varepsilon_D - \varepsilon_A)t} \cdot \sum_k \frac{\left(+D_\alpha e^{-i\omega_\alpha t}\right)^k}{k!}$$

No surprise,
Fermi's Golden Rule

$$= \frac{|J|^2}{\hbar^2} \cdot e^{-D_\alpha} \cdot \sum_k \frac{(+D_\alpha)^k}{k!} \cdot \int_{-\infty}^{\infty} dt \cdot e^{\frac{i}{\hbar}(\varepsilon_D - \varepsilon_A - k\hbar\omega_\alpha)t}$$

$$= \frac{|J|^2}{\hbar^2} \cdot \boxed{e^{-D_\alpha} \sum_k \frac{D_\alpha^k}{k!}} \cdot \delta(\varepsilon_D - \varepsilon_A - k\hbar\omega_\alpha)$$

F-C factor

This yields a rate determined by Franck-Condon factors ⇒ electronic coupling modified by F C factor, vibrational overlap!

$$J_{A\nu_1; D\nu_2} = \langle A\nu_1 | H | D\nu_2 \rangle$$
$$= \langle A | H | D \rangle \cdot \langle \nu_1 | \nu_2 \rangle$$

evaluating the sum yields quantum rate.

This does not tell us specifically the dependence of the quantum rate as a function of energy gap, $\varepsilon_D - \varepsilon_A$, so we try to evaluate the integral approximately.

⇒ notice that the exponent

$f(t)$ has a fast oscillating factor due to $e^{-i\omega_\alpha t}$ when $\omega_\alpha \gg 1$.

(This part is due to Schatz & Ratner)

We can evaluate the integral using the stationary ~~ph~~ phase / steepest descent technique. We approximate as

$$\int_{-\infty}^{\infty} dt \cdot e^{f(t)} \cong \int_{-\infty}^{\infty} dt \cdot \exp\left\{ f(t=t_s) + \left.\frac{\partial f}{\partial t}\right|_{t=t_s} (t-t_s) + \frac{1}{2}\left.\frac{\partial^2 f}{\partial t^2}\right|_{t_s} (t-t_s)^2 \right\}$$

~~by~~ at the saddle point t_s so that

$$\int_{-\infty}^{\infty} dx_1\, e^{-\frac{x^2}{2\sigma^2}} = \sqrt{2\pi}\cdot\sigma$$

$$\left.\frac{\partial f}{\partial t}\right|_{t=t_s} = 0 .$$

∴ ~~$f(t) \approx \frac{\varepsilon}{\hbar}$~~ simple.

⇒ became a Gaussian integral,

$$\int_{-\infty}^{\infty} dt\, e^{f(t)} \simeq e^{f(t_s)} \cdot \sqrt{\frac{2\pi}{\left| \partial^2 f / \partial t^2 \right|_{t=t_s}}}$$

here $f(t) = \frac{i}{\hbar}(\varepsilon_0 - \varepsilon_A)t + D_\alpha \cdot e^{-i\omega_\alpha t}$.

$$\therefore \left. f'(t)\right|_{t=t_s} = \frac{i}{\hbar}(\varepsilon_0 - \varepsilon_A) - iD_\alpha \cdot \omega_\alpha \cdot e^{-i\omega_\alpha t_s} = 0$$

$e^{-i\omega_\alpha t_s} = \frac{\varepsilon_0 - \varepsilon_A}{\hbar D_\alpha \omega_\alpha}$, ~~$t_s$~~ ⇒ also defines (imaginary) ti

(13)

valid only when $\varepsilon_D > \varepsilon_A$

Note that t_s is purely imaginary; $-it_s = \frac{1}{\omega_\alpha} \ln \frac{\varepsilon_D - \varepsilon_A}{D_\alpha \hbar\omega_\alpha}$

$$\therefore k_{A\leftarrow D} \cong \frac{|J|^2}{\hbar^2} \cdot e^{-D_\alpha} \cdot e^{f(t_s)} \cdot \sqrt{\frac{2\pi}{\left|\partial^2 f/\partial t^2\right|_{t=t_s}}}$$

$\varepsilon_D > \varepsilon_A$

neglect the prefactors & terms independent of λ_α

$$\varepsilon_D - \varepsilon_A \Rightarrow f(t_s) = \frac{\varepsilon_D - \varepsilon_A}{\hbar} \cdot it_s + D_\alpha \cdot e^{-i\omega_\alpha t_s} = \frac{\varepsilon_D - \varepsilon_A}{\hbar\omega_\alpha}\left(\ln \frac{\hbar D_\alpha \omega_\alpha}{\varepsilon_D - \varepsilon_A} + 1\right)$$

$$e^{f(t_s)} = e^{\frac{\varepsilon_D - \varepsilon_A}{\hbar\omega_\alpha} \times \left(\ln \frac{\lambda_\alpha}{\varepsilon_D - \varepsilon_A} + 1\right)}$$

weak $\varepsilon_D - \varepsilon_A$ dependence.

$$\hat{=}\ e^{-\left(\frac{\varepsilon_D - \varepsilon_A}{\hbar\omega_\alpha}\right) \cdot \gamma}$$

note that $-\gamma = \ln \frac{\lambda_\alpha}{\varepsilon_D - \varepsilon_A} + 1$.

is negative into the inverted regime $\varepsilon_D - \varepsilon_A > \lambda_\alpha$

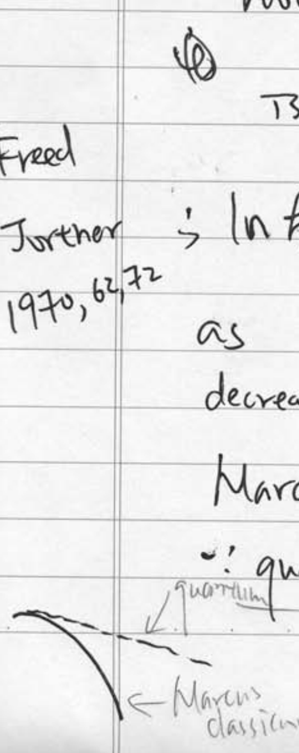
Karl Freed & J. Jortner JCP 1970, 62, 72

$$\therefore \ln k_{A\leftarrow D} \sim k_0 - \frac{(\varepsilon_D - \varepsilon_A)}{\hbar\omega_\alpha} \cdot \gamma$$

as $\varepsilon_D - \varepsilon_A \equiv -\Delta G^0$ ~~goes more negative~~ increases ~~the~~ $\ln k$ decreases linearly !! ~~(Marcus theory says qu~~

Marcus theory says quadratically !!

$\therefore$ quantum theory rate slow down less.



This is a case of the energy gap law of radiationless decay.

timeless