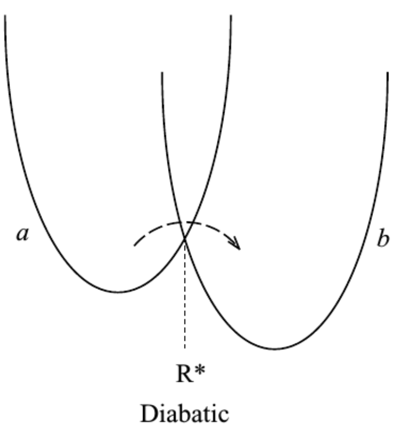
Marcus Theory of Electron Transfer

The Nobel Prize in Chemistry 1992

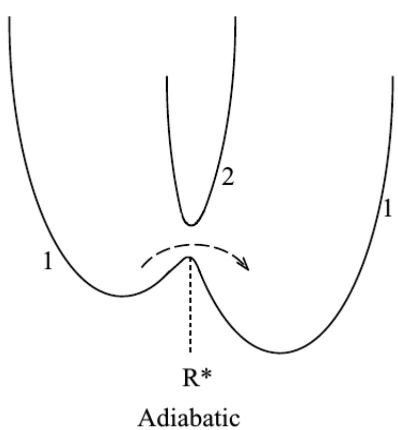
for his contributions to the theory of electron transfer reactions in chemical systems; however the full scope of Marcus Theory is much broader and can be used in all condensed matter.

$$k_{ET} = Z_{ab} \exp\left\{ -\frac{(\Delta G^0_{ab} + \lambda)^2}{4\lambda k_B T} \right\}$$

Rudolph A. Marcus



weak electronic coupling



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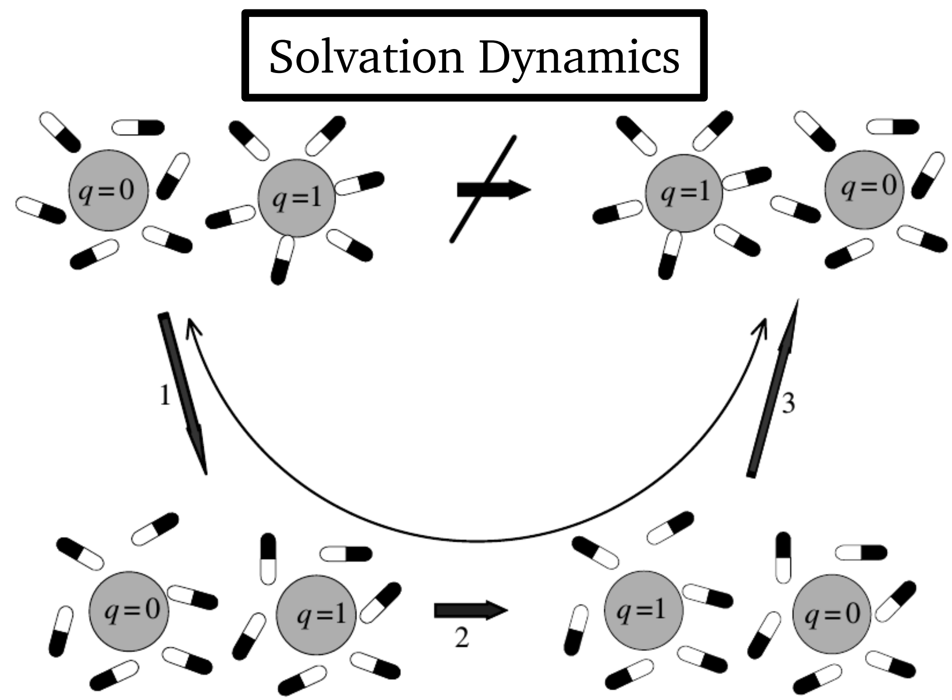

adapted from *Chemical Dynamics in Condensed Phases*, A. Nitzan, Oxford Press.

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$$k_{ET} = \frac{2\pi}{\hbar}|V_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{\left(\Delta G^0_{ab} + \lambda\right)^2}{4\lambda k_B T}\right\}$$

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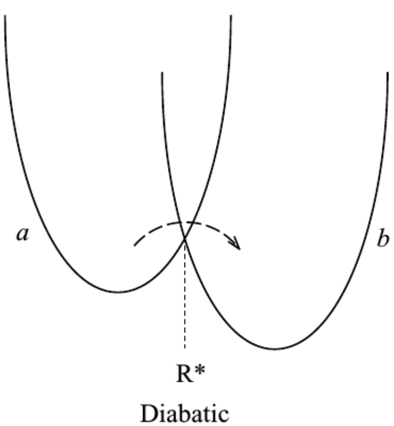

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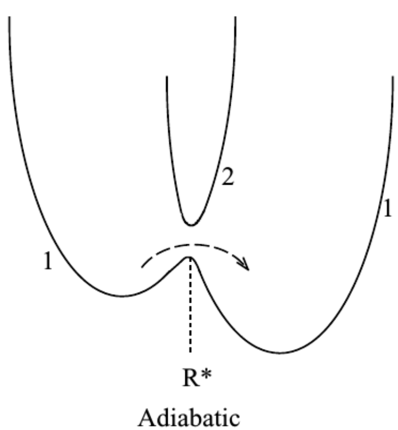

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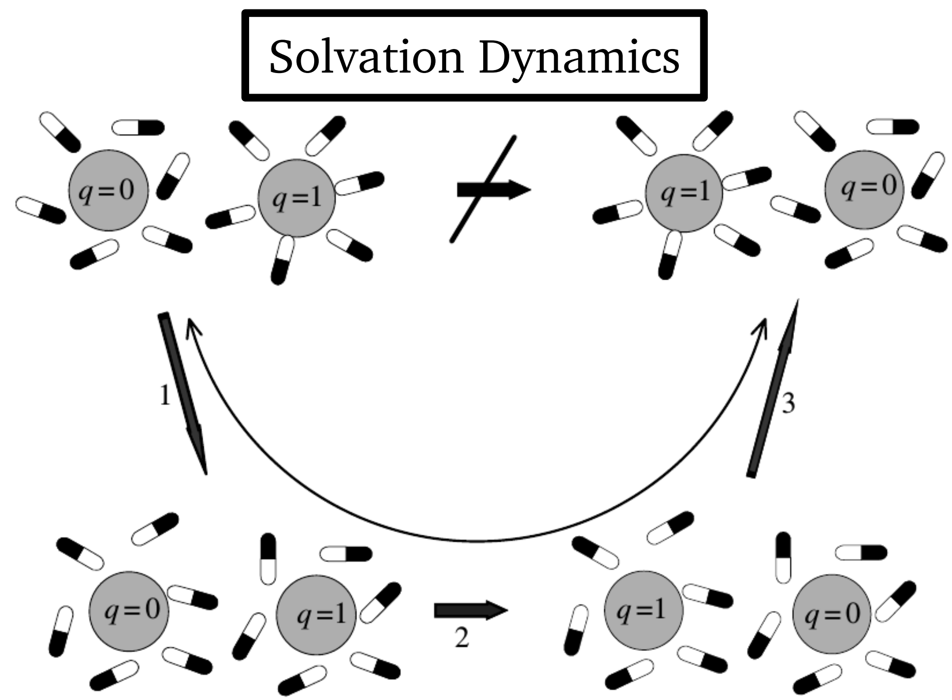

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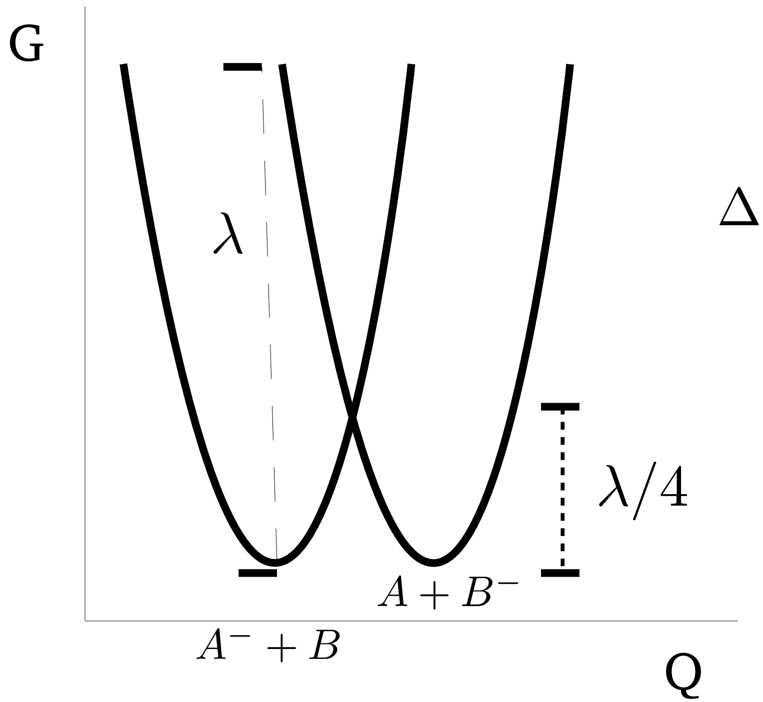
$$\frac{2\pi}{\hbar}|V_{ab}|^2 \quad = \quad \text{collision frequency} \ \sim 10^{-9} - 10^{-10}\ \text{sec}^{-1}$$

$$\Delta G^0_{ab} \quad = \quad \text{free energy change for the ET}$$

The Marcus Parabolae:



$$\Delta G^0 = 0 \Longrightarrow \exp\left\{-\frac{\left(\Delta G^0_{ab} + \lambda\right)^2}{4\lambda k_B T}\right\} = e^{-\frac{\lambda/4}{k_B T}}$$

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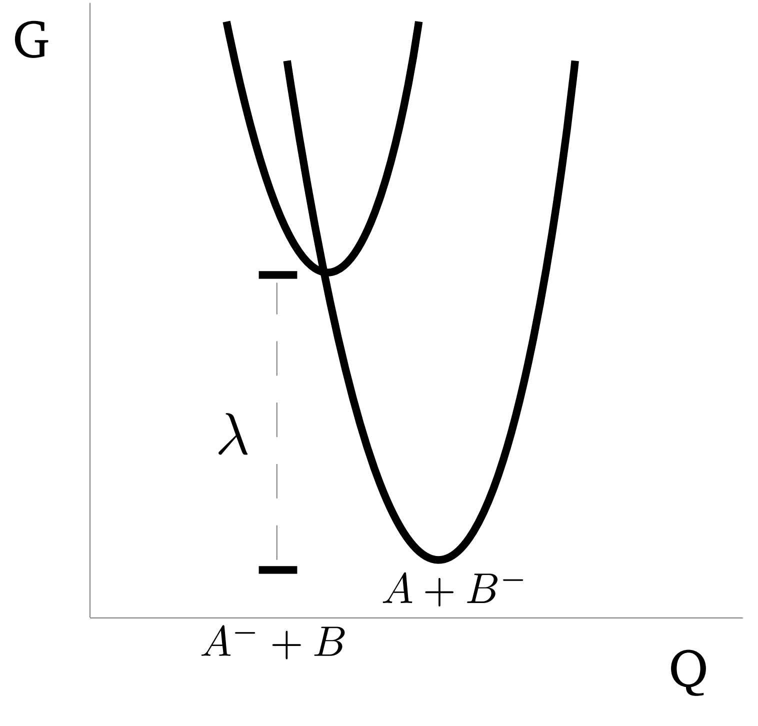

exergonic (spontaneous) reaction:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} < 0$$

$$\Delta G^0_{ab} = -\lambda$$

$$\Longrightarrow \exp\left\{-\frac{\left(\Delta G^0_{ab}+\lambda\right)^2}{4\lambda k_B T}\right\} = e^{-\frac{0}{k_B T}} = 1$$

diffusion controlled

Marcus Theory of Electron Transfer

$$k_{ET} = \frac{2\pi}{\hbar}|V_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{\left(\Delta G^0_{ab} + \lambda\right)^2}{4\lambda k_B T}\right\}$$

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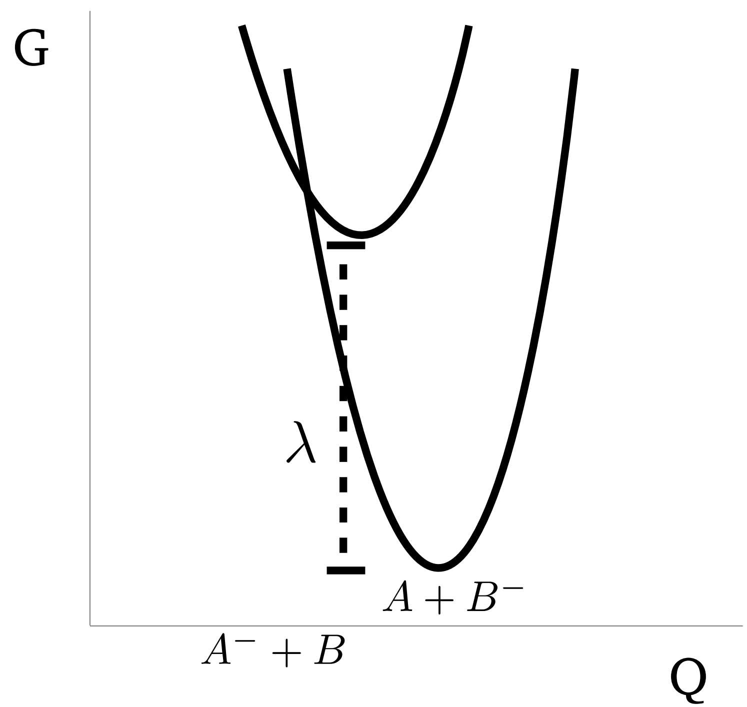


exergonic (spontaneous) reaction:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} < 0$$

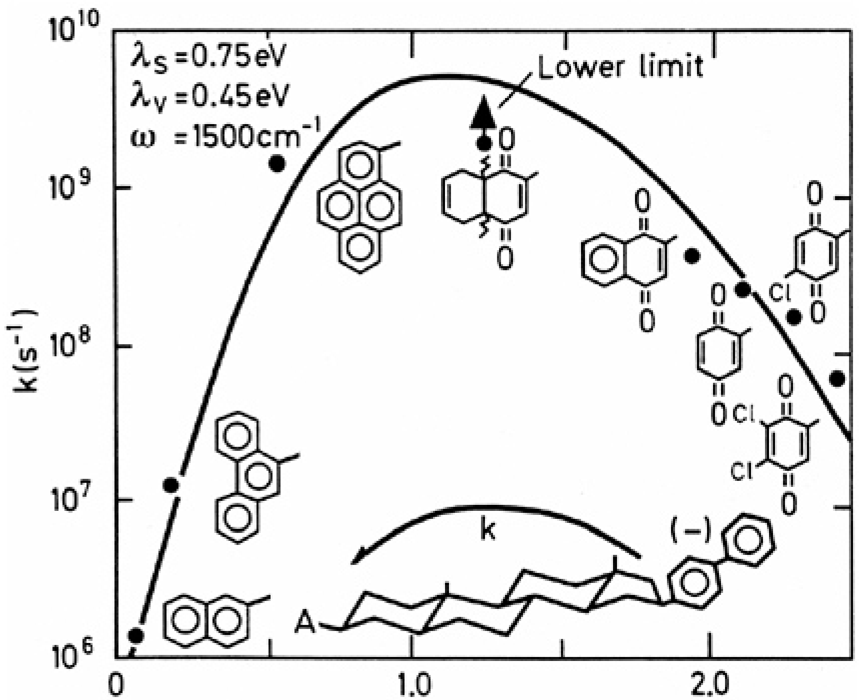
$$|\Delta G^0_{ab}| > \lambda$$

$$\Longrightarrow \exp\left\{-\frac{\left(\Delta G^0_{ab} + \lambda\right)^2}{4\lambda k_B T}\right\} < 1$$

Inverted region: $k_{ET} < k_{max}$

Marcus Theory of Electron Transfer

$$k_{ET} = \frac{2\pi}{\hbar}|V_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left\{ -\frac{\left(\Delta G^0_{ab} + \lambda\right)^2}{4\lambda k_B T} \right\}$$



- $\Delta G^0 (eV)$

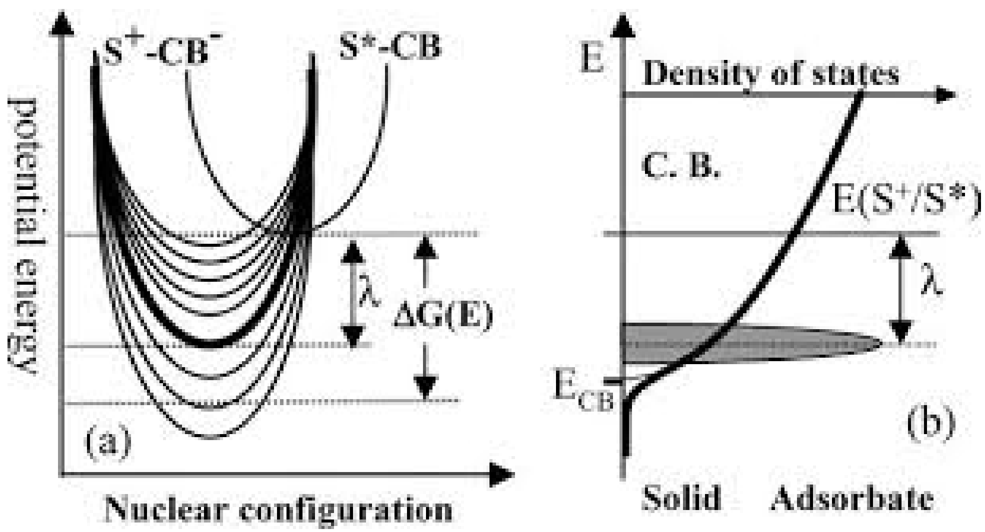
G. L. Closs and J. R. Miller. “*Intramolecular long-distance electron transfer in organic molecules*”. Science 240(1988):440-47.

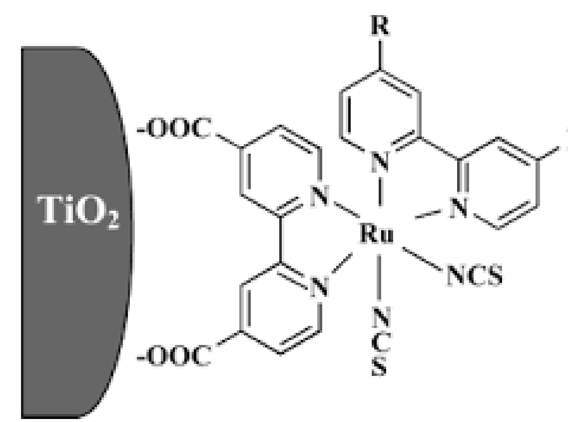
Marcus Theory of Electron Transfer

Extensions to the original Marcus theory:

- ***strong electronic coupling: Marcus-Hush theory***
  the inner sphere electron transfer theory of Noel S. Hush refers to a continuous change of the electron density during transfer along a geometrical coordinate (adiabatic case).

- ***Interfacial Elctron Transfer:***





N. A. Anderson, T. Lian, “Ultrafast electron transfer at the molecule-semiconductor nanoparticle interface”, Annu. Rev. Phys. Chem. 2005. 56:491–519.

- ***Coupled Electron and Proton Transfer:***

S. Hammes-Schiffer, A. Stuchebrukhov, “Theory of Coupled Electron and Proton Transfer Reactions”, Chem. Rev. 2010. 110, 6930..

to be continued ...