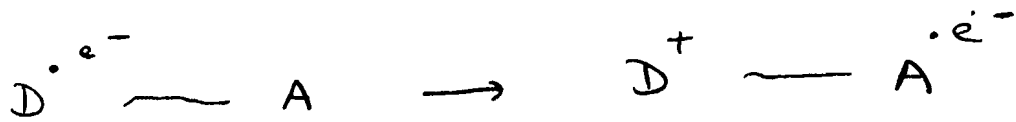


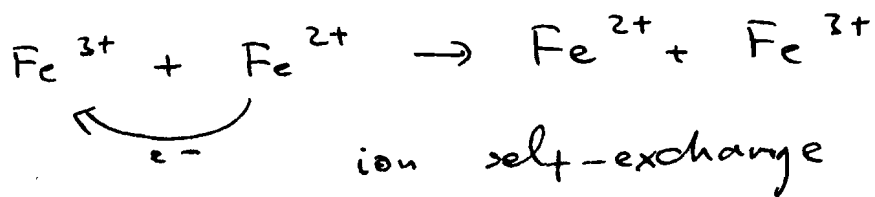
Time-independent perturbations and Chemistry:

transport of electrons

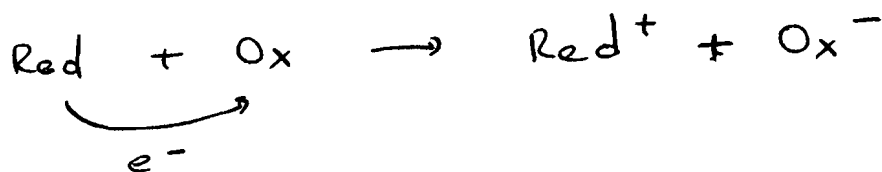
Many problems in chemistry and Biology involve changing electronic charge distribution or moving electrons from one particle (electron donor, D) to another particle (electron acceptor, A):



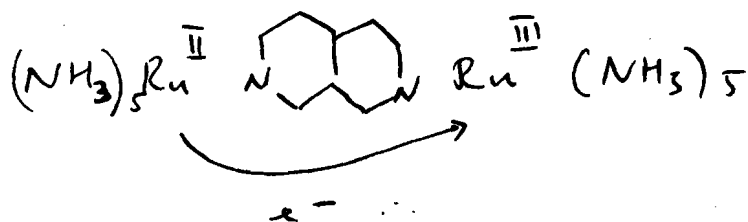
Examples:



Any redox reaction:

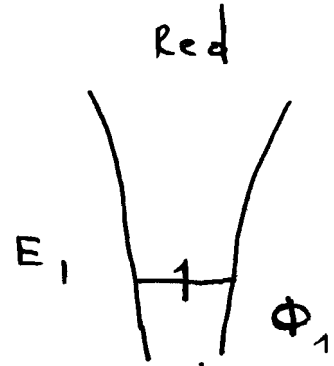
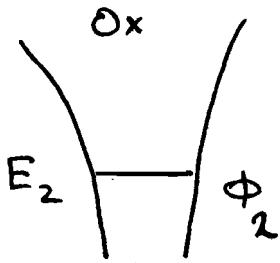


Binuclear complexes:



How do we approach this class of problems?

Let's assume Red and Ox species at infinite distance



Empty state: E_2, ϕ_2

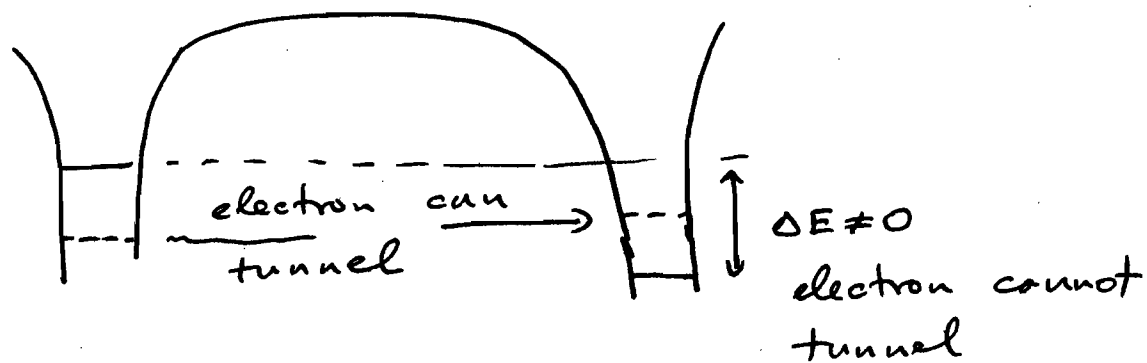
Occupied state: E_1, ϕ_1

At $R \rightarrow \infty$, there is no interaction between Red and Ox and states E_1 and E_2 are stationary, their occupations do not change

When Red starts to approach Ox, there will appear an interaction between them V , which is stationary, i.e. does not depend on time. The Fermi's Golden Rule then suggests a transition probability

$$W_{12} = \frac{2\pi}{\hbar} |\langle \phi_1 | V | \phi_2 \rangle|^2 \delta(E_1 - E_2)$$

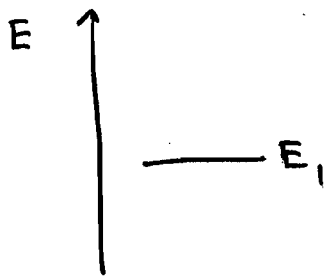
This equation requires energy conservation: $E_1 = E_2$



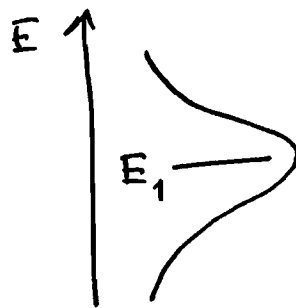
The energy required for tunneling is provided by thermal motions, i.e. by the bath of phonons. Fluctuations of the environment create potential fluctuations at the position of the electron:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Phi(\vec{r}) - e\delta\varphi \Phi(\vec{r}) = [E - e\delta\varphi] \Phi(\vec{r})$$

The localized energy level gains distribution:



without thermal fluctuations



with thermal fluctuations

Because of the thermal noise, the rate of E-Y electronic transitions becomes

$$W_{12} = \frac{2\pi}{\hbar} |V_{12}|^2 \langle \delta(E_1 - E_2) \rangle$$

$\langle \Phi_1 | V | \Phi_2 \rangle$
average over the Boltzmann distribution of thermal fluctuations

Linear coupling model (Marcus' 56) assumes a linear coupling of $\Delta E = E_1 - E_2$ to fluctuations of the potential represented by a Gaussian noise:

$$E_1 - E_2 = \langle \Delta E \rangle - a \delta\varphi$$

$$\langle E_1 - E_2 \rangle = \langle \Delta E \rangle$$

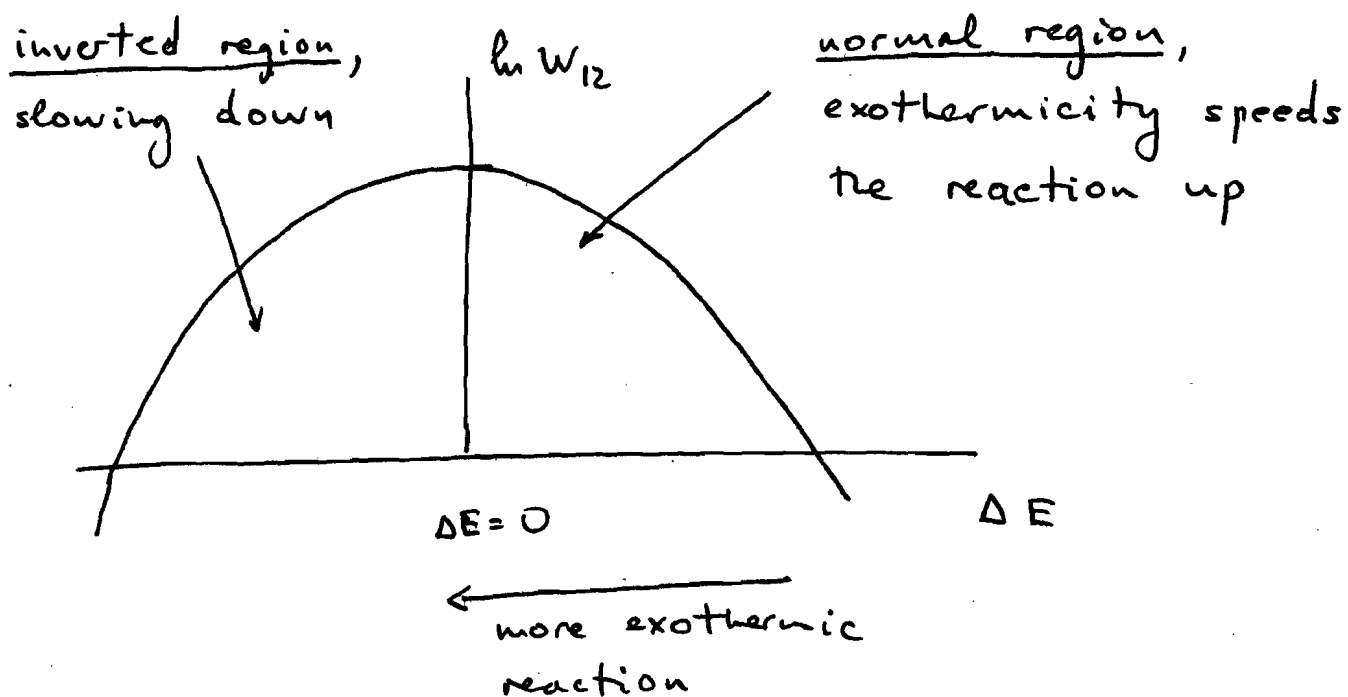
$$\langle \delta(E_1 - E_2) \rangle = \frac{\int \delta(\langle \Delta E \rangle - a\delta\varphi) e^{-\frac{(\delta\varphi)^2}{2\alpha KT}} d(\delta\varphi)}{\int e^{-\frac{(\delta\varphi)^2}{2\alpha KT}} d(\delta\varphi)} =$$

$$= \frac{1}{\sqrt{2\pi\alpha KT}} \frac{1}{a} \exp\left[-\frac{\langle \Delta E \rangle^2}{2a^2\alpha KT}\right]$$

$$W_{12} = \frac{2\pi |V_{12}|^2}{\hbar} \left(\frac{1}{2\pi a^2 \kappa kT} \right)^{1/2} \exp \left[- \frac{\langle \Delta E \rangle^2}{2a^2 \kappa kT} \right]$$

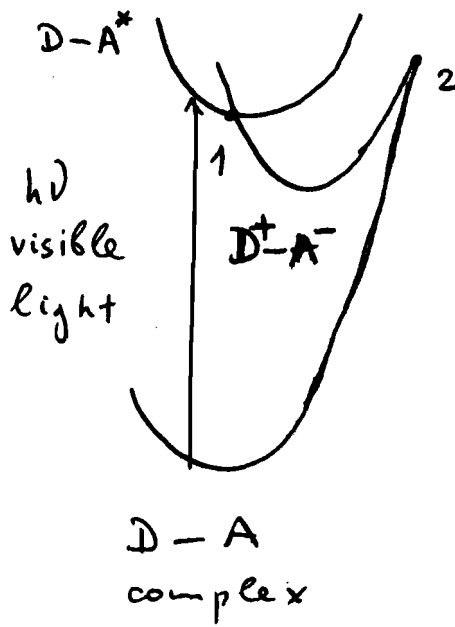
$\lambda = \frac{1}{2} a^2 \kappa \leftarrow$ reorganization energy

The rule "the more downhill, the faster you go" is not correct, inverted region



$\langle \Delta E \rangle$ is typically decreased by making the reaction Gibbs energy more negative, more exothermic.

How photosynthesis works?



- x Visible light excites the donor-acceptor complex (D-A) into a state of higher energy
- x Electron is transferred from D to A on a ps time-scale without activation barrier (point 1)
- x The state D^+A^- can live sufficiently long for useful chemistry to happen. The reason is that point 2 is in the inverted region and the reaction $D^+A^- \rightarrow DA$ is slow despite a strongly negative reaction free energy... for recombination