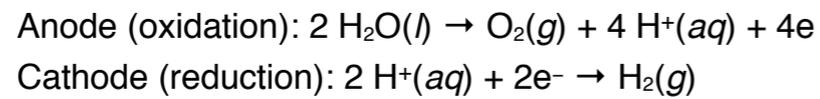
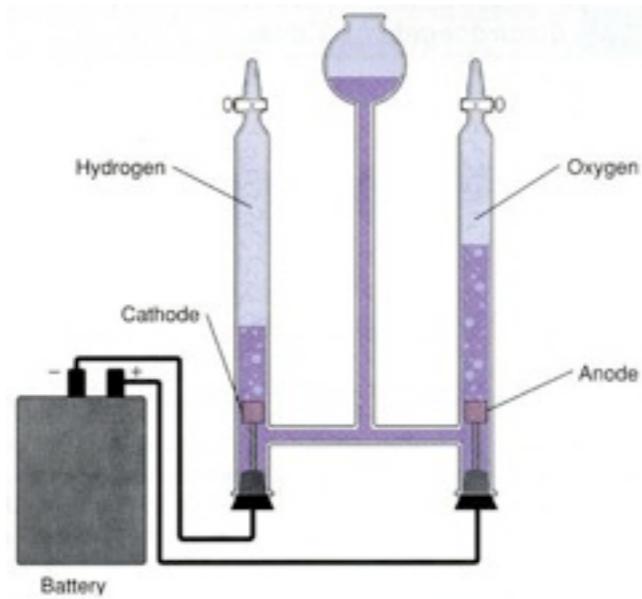


# Theory of electron transfer

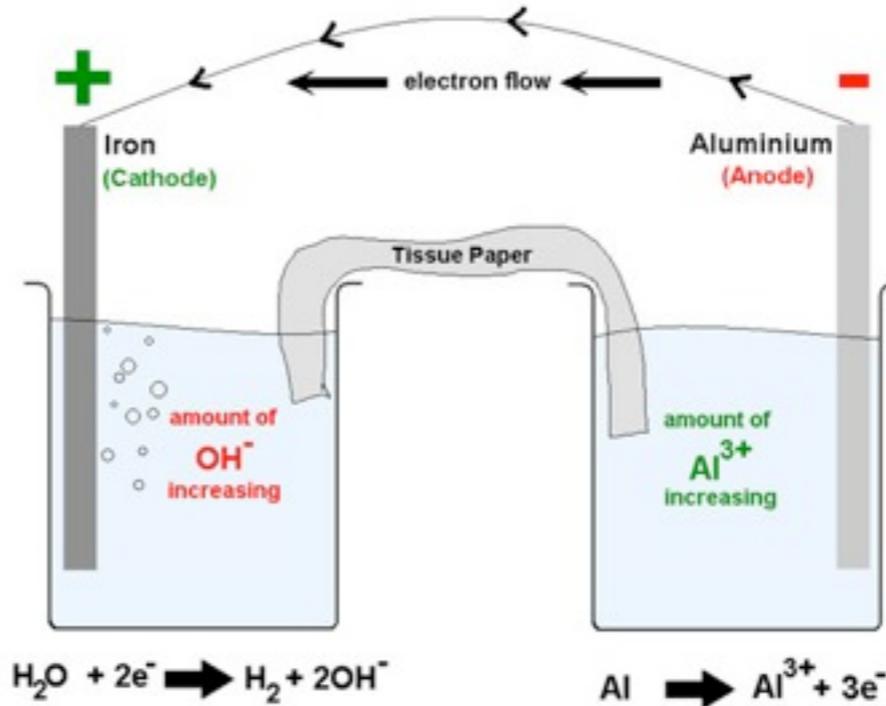
Winterschool for Theoretical Chemistry and Spectroscopy  
Han-sur-Lesse, Belgium, 12-16 December 2011

# Electron transfer

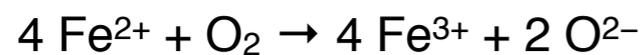
## Electrolyse



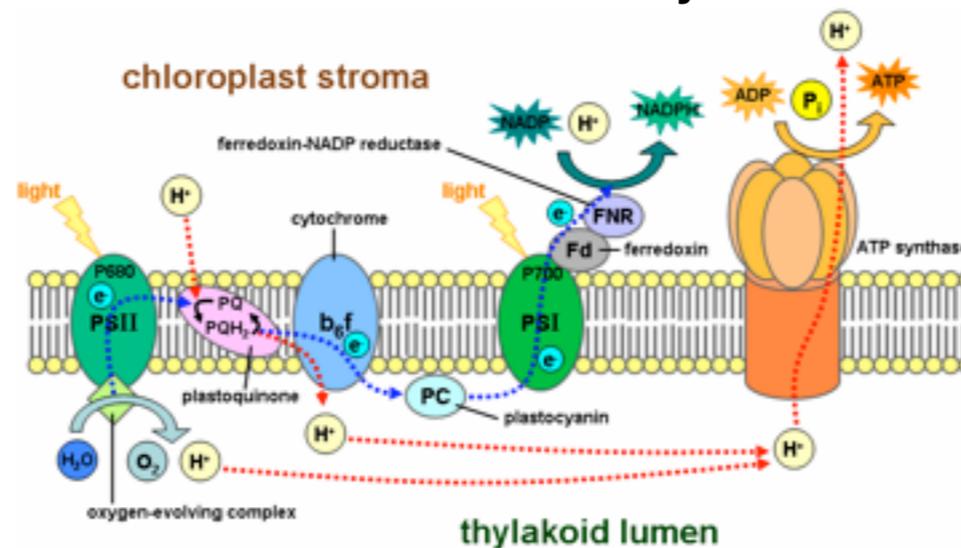
## Battery



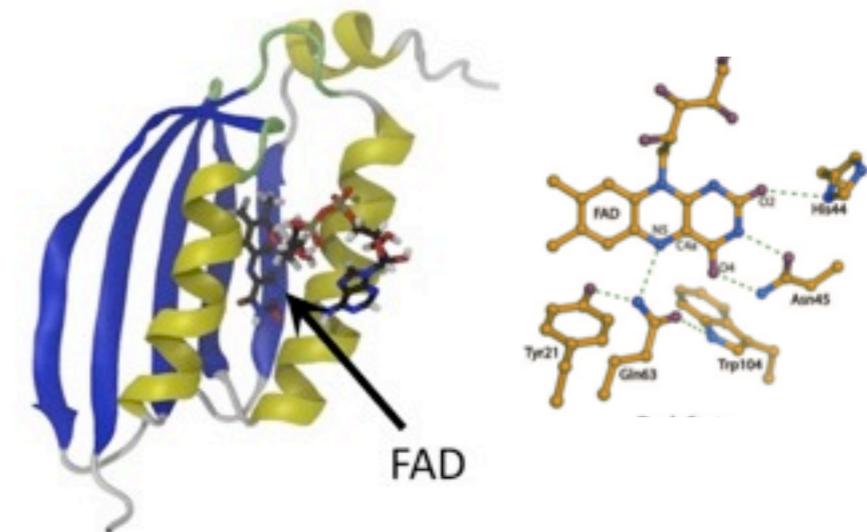
## Redox reactions



## Electron transfer system



## Photoactive proteins

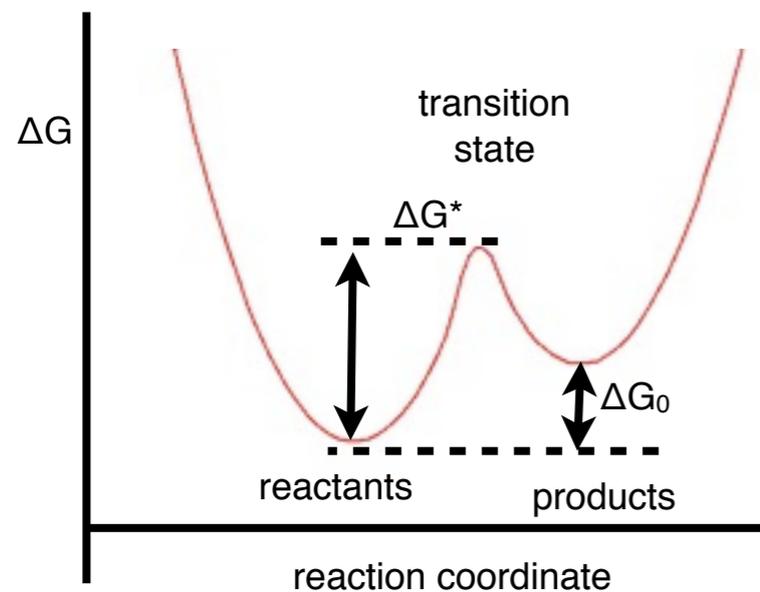
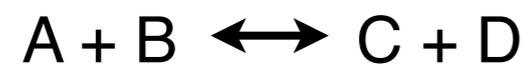


# Electron transfer

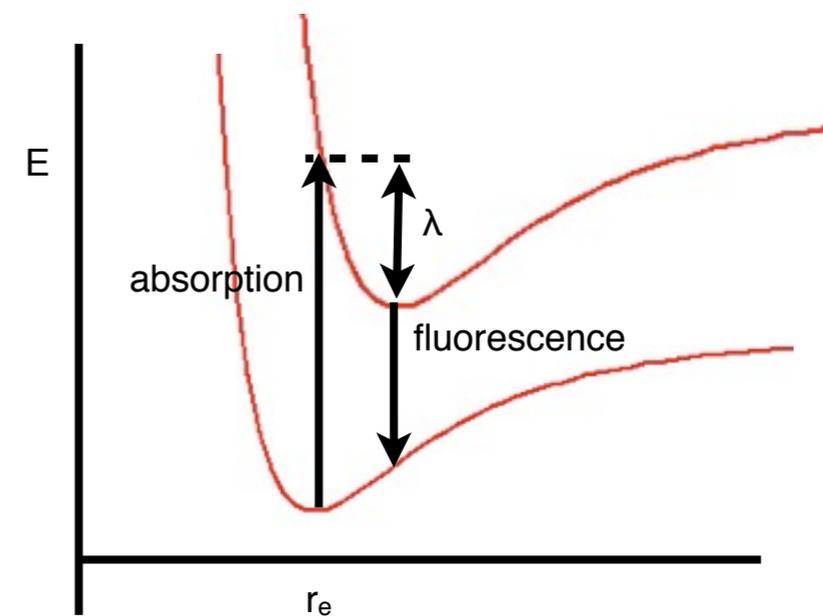


electron transfer

chemical reaction



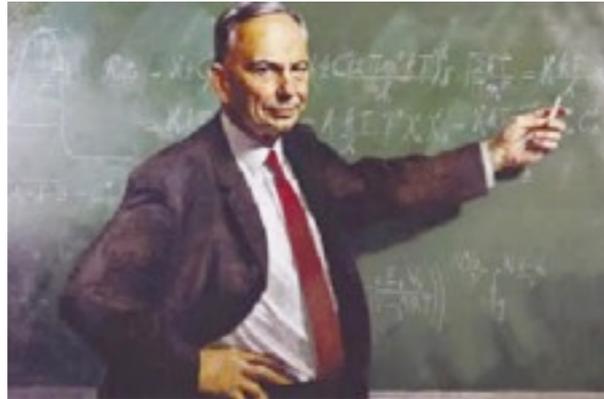
electronic excitation



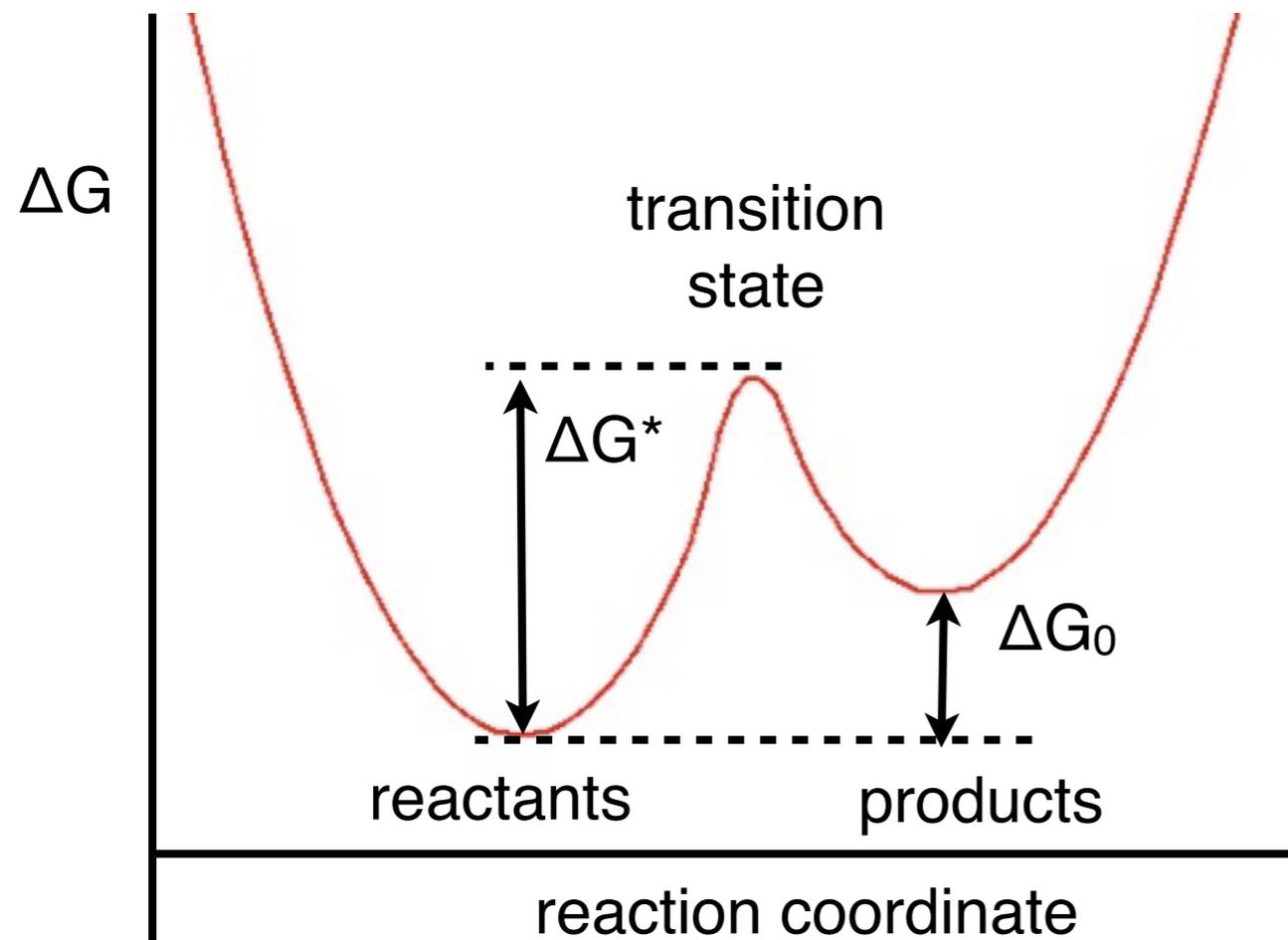
# Chemical reaction



Svante Arrhenius  
1859-1927  
1903 Nobel prize



Henry Eyring  
1901-1981



## Arrhenius equation

$$k_{RS \rightarrow PS} = k_0 e^{-\beta \Delta G^*}$$

## Final equilibrium

$$\begin{aligned} K &= \frac{[D^+][A^-]}{[D][A]} = \frac{k_{RS \rightarrow PS}}{k_{PS \rightarrow RS}} \\ &= \frac{k_0 e^{-\beta(G_{TS} - G_{RS})}}{k_0 e^{-\beta(G_{TS} - G_{PS})}} \\ &= e^{-\beta \Delta G_0} \end{aligned}$$

# Franck Condon principle



James Franck  
1882-1964  
1925 Nobel prize

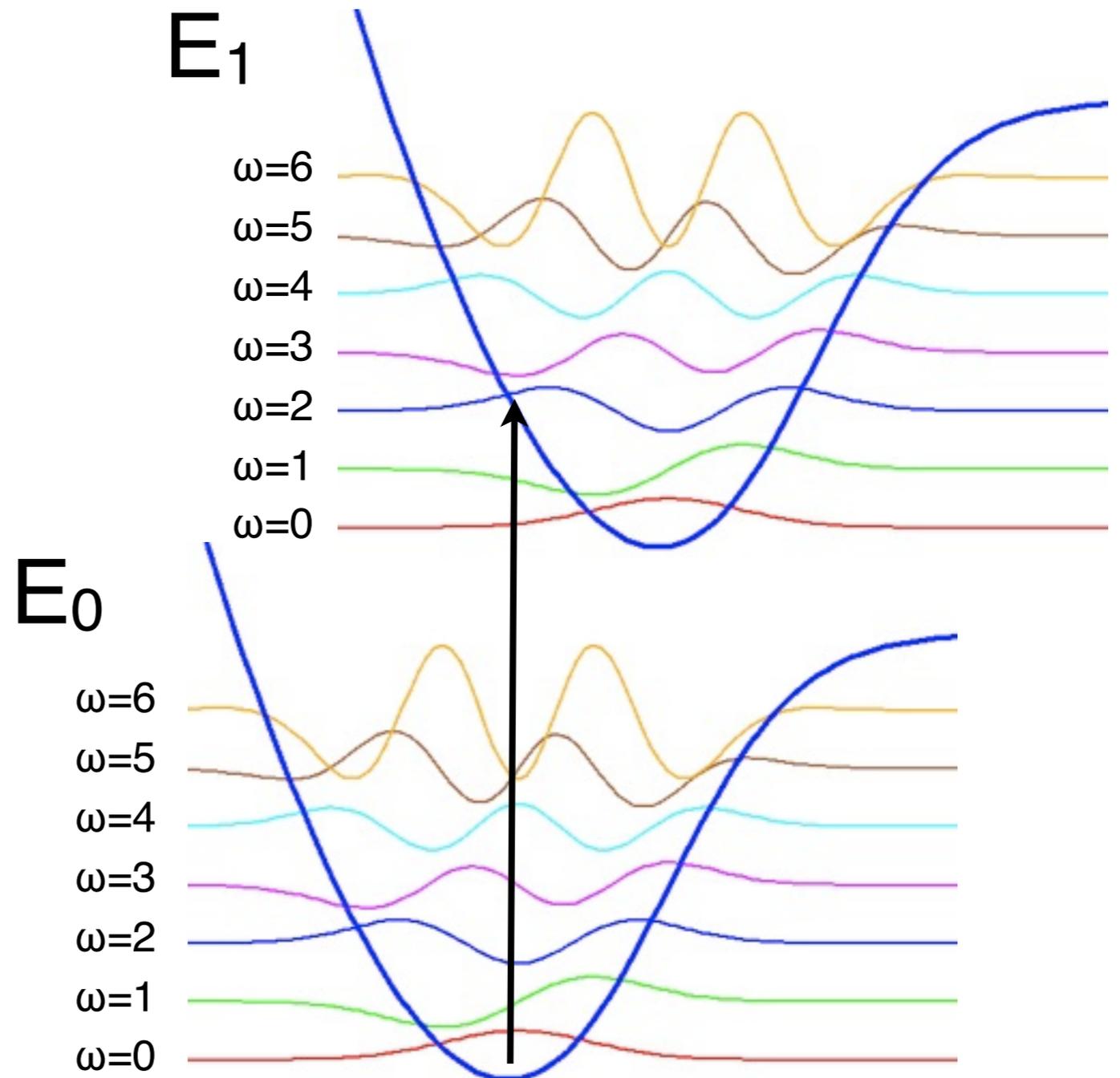


Edward Condon  
1902-1974

The probability (or amplitude) of a simultaneous electronic and vibrational transition to a new “vibronic” state depends on the overlap between the wavefunctions of the ground and excited states.

Or:

Electrons move much faster than nuclei. For an electronic excitation to occur, the nucleic configuration should be optimal (the same).



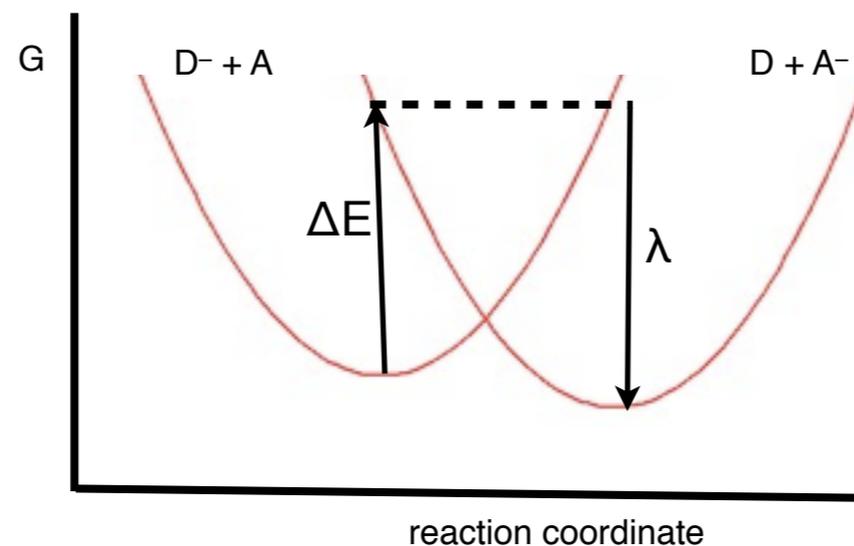
# Marcus theory of electron transfer

## Not quite as the Chemical Reaction picture

- The transfer of the electron is not a good reaction coordinate; it is not the slow variable.

## Not quite as the Franck-Condon picture

- Vertical excitation does not conserve energy; electron transfer reactions also occur in the dark.



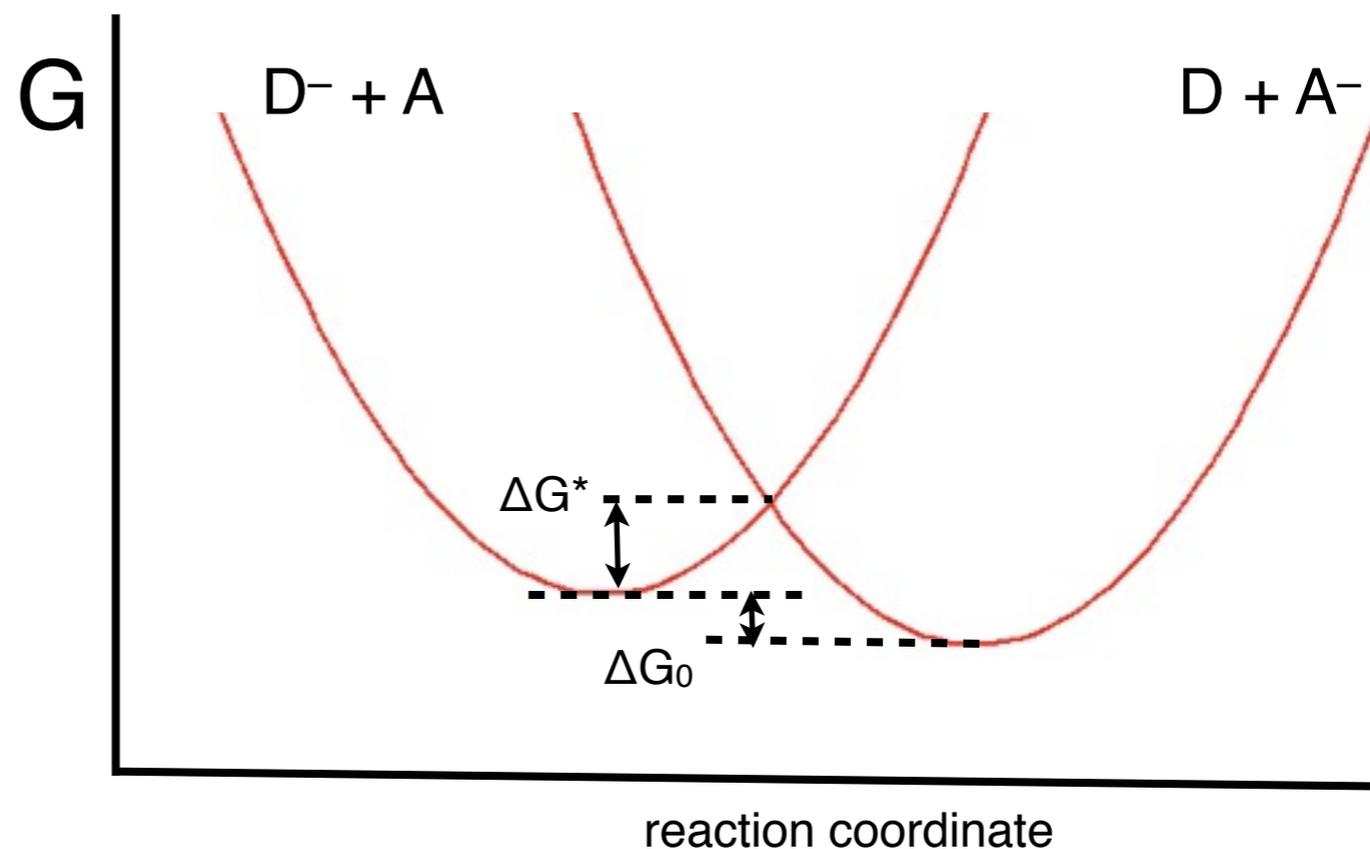
# Contents

Marcus theory of electron transfer

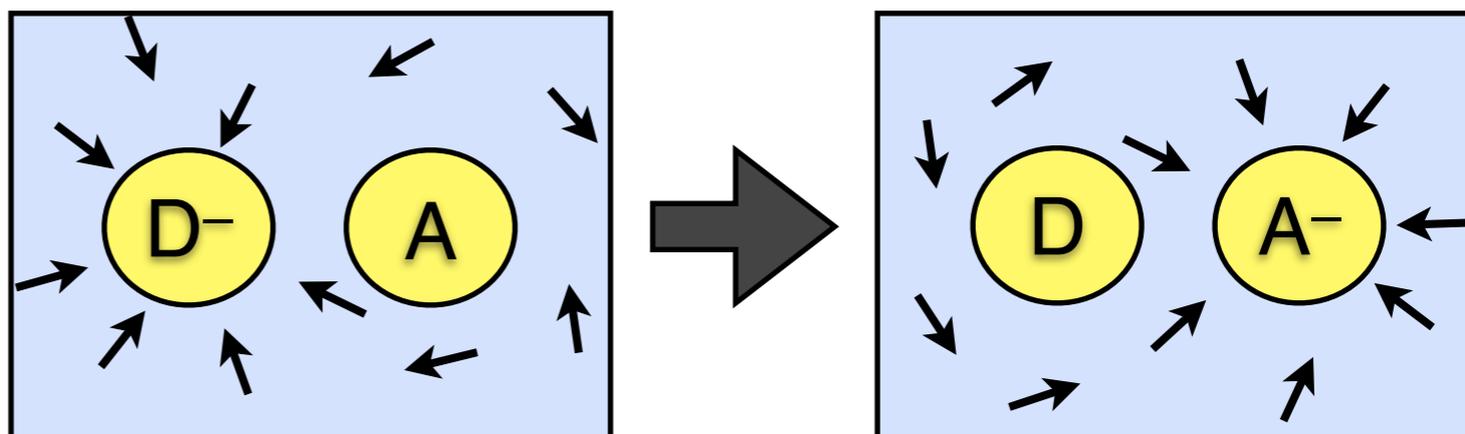
# Marcus theory of electron transfer



Rudolph A. Marcus (1923)  
1992 Nobel prize



The reaction coordinate is a measure of the amount of charge that is transferred. It is also a measure of the response (polarization) of the dielectric environment (solvent).



# Marcus idea

## Classical electrostatic model

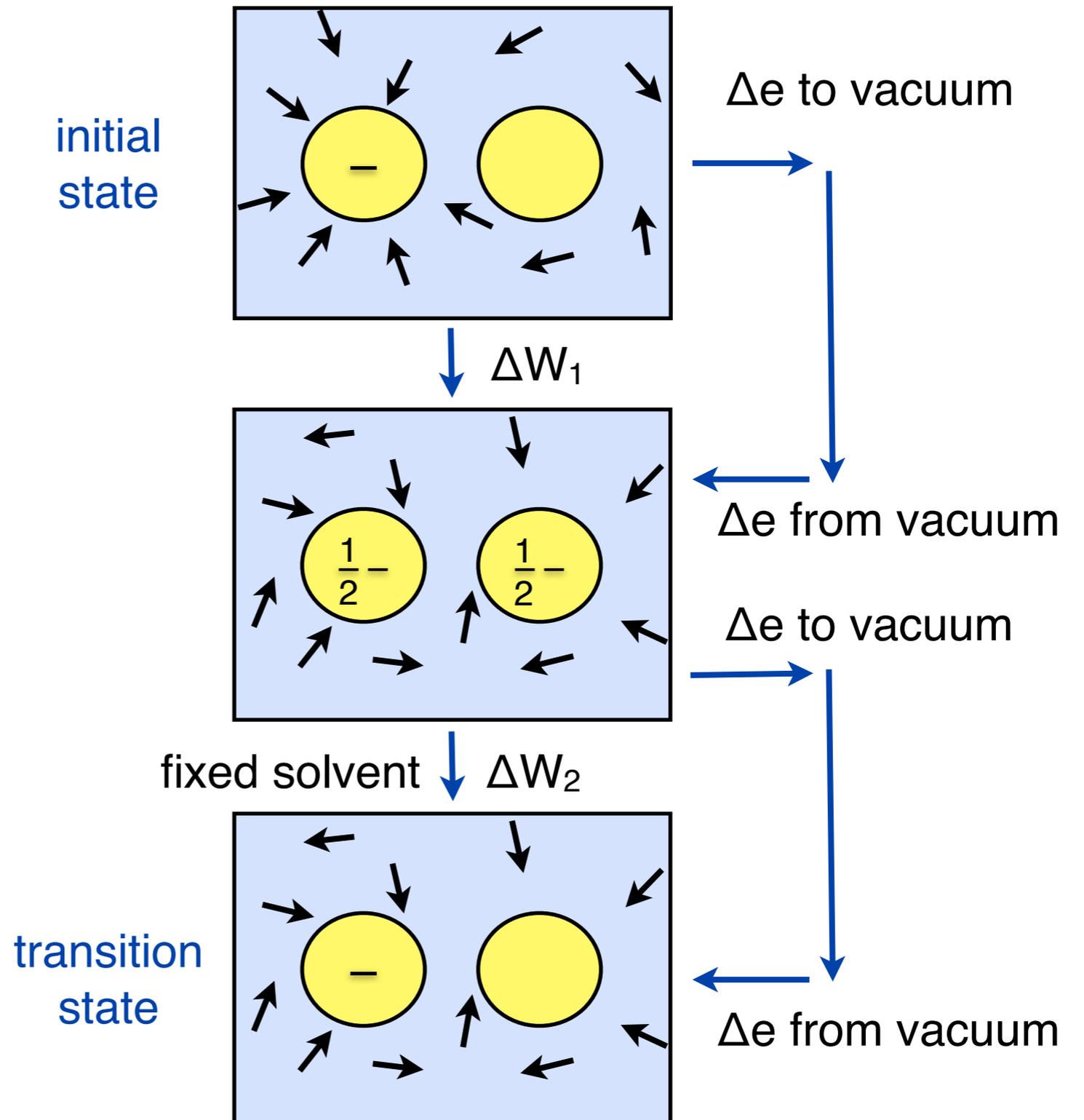
Take a charged and neutral sphere in a dielectric medium.

Step 1: move half an electron to reach a symmetric system.

The work  $\Delta W_1$  is due to the electric field on the solvent which creates an electronic and configurational polarization,  $P_e + P_c$

Step 2: move half an electron back, but maintain the atom configuration fixed. Only the electronic polarization adapts.

The Gibbs free energy to reach this (non-equilibrium) transition state is  $\Delta W_1 + \Delta W_2$



# Marcus idea

## Classical electrostatic model

The complicated reaction coordinate involving all solvent atom coordinates is replaced by a single coordinate: the solvent polarization.

The gibbs free energy can this way be calculated for any arbitrary charge transfer.

$$\Delta G = \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R_{12}} \right) \cdot \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \cdot (\Delta e)^2$$

$r_1, r_2$  : sphere radii

$R_{12}$  : distance between spheres

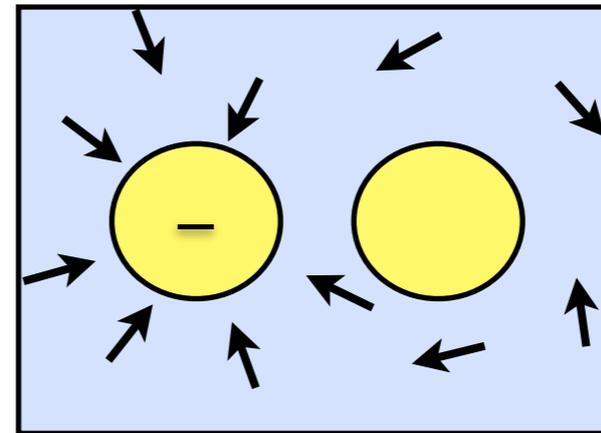
$\epsilon_{op}$  : optical dielectric constant

$\epsilon_s$  : static dielectric constant

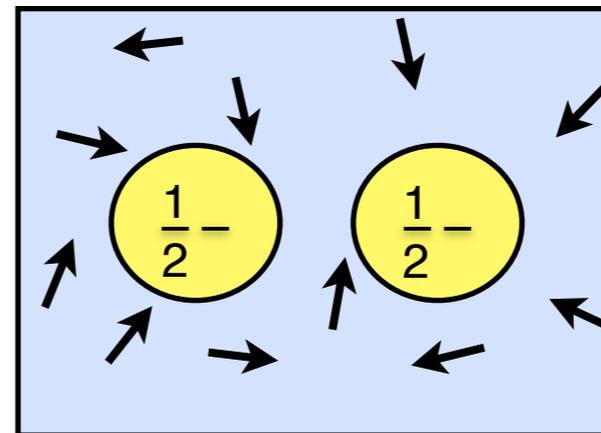
$\Delta e$  : amount of charge transfered

The free energy profile is a parabola.

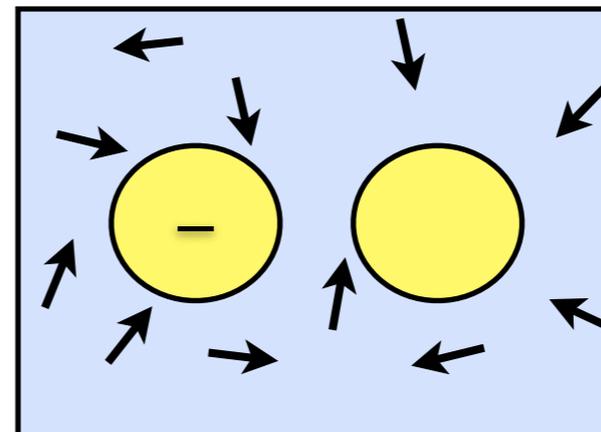
initial  
state



$\Delta W_1$



fixed solvent  $\Delta W_2$



transition  
state

$\Delta e$  to vacuum

$\Delta e$  from vacuum

$\Delta e$  to vacuum

$\Delta e$  from vacuum

# Gaussian potentials

To move to a microscopic, atomistic, picture, the spheres could represent a ligated metal ion, such as in:



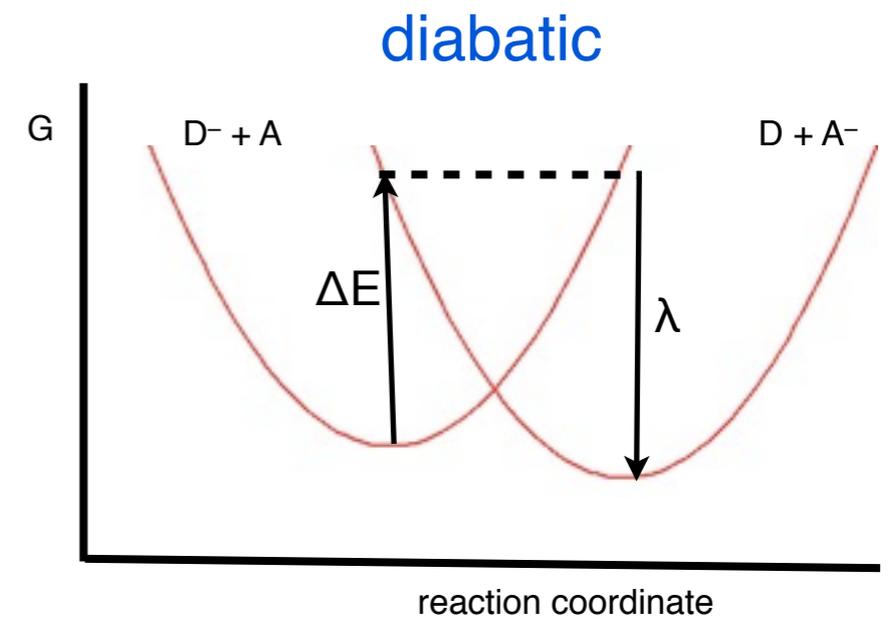
Although, we cannot transfer a partial electron charge, the previous theory still holds, if we consider the reaction coordinate to be the polarization due to a hypothetical  $\Delta e$ . (Outer sphere ET)

The polarization response of a charged species by an environment continuously fluctuates. The fluctuations can be assumed Gaussian statistics, as they are the sum of many uncorrelated solvent interactions (central limit theorem).

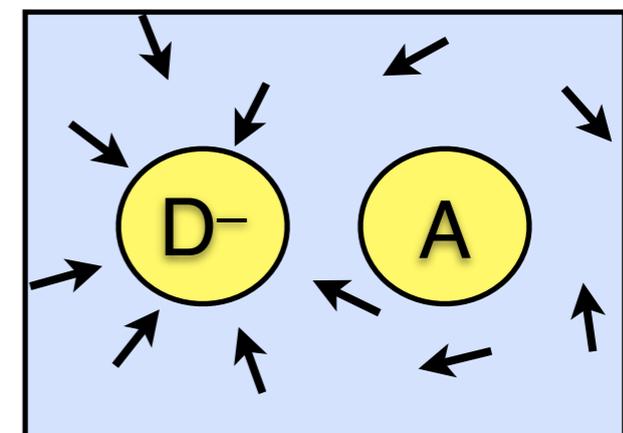
If the two states  $|D^-+A\rangle$  and  $|D+A^-\rangle$  are very weakly coupled, we can treat them as separate states along the reaction coordinate. The activation energy is governed by that rare polarization event as if half an electron was transferred. The electron can then instantaneously jump.

Note that the transition state is not a single configuration.

## Classical electrostatic model



## Reactant state





WIKIPEDIA  
The Free Encyclopedia

Article [Discussion](#)

# Central limit theorem

From Wikipedia, the free encyclopedia

## Central limit theorems for independent sequences

### Classical CLT

[\[edit\]](#)

Let  $\{X_1, \dots, X_n\}$  be a **random sample** of size  $n$ —that is, a sequence of **independent and identically distributed** random variables with **expected values**  $\mu$  and **variances**  $\sigma^2$ .

Suppose we are interested in the behavior of the **sample average** of these random variables:  $S_n := (X_1 + \dots + X_n)/n$ . Then the central limit theorem asserts that as  $n$  gets larger, the distribution of  $S_n$  approximates **normal** with mean  $\mu$  and variance  $\frac{1}{n}\sigma^2$ . The true strength of the theorem is that  $S_n$  approaches normality regardless of the shapes of the distributions of individual  $X_i$ 's. Formally, the theorem can be stated as follows:

**Lindeberg–Lévy CLT:** suppose  $\{X_j\}$  is a sequence of **iid** random variables with  $E[X_j] = \mu$  and  $\text{Var}[X_j] = \sigma^2$ . Then as  $n$  approaches infinity, the random variable  $\sqrt{n}(S_n - \mu)$  **converges in distribution** to a **normal**  $N(0, \sigma^2)$ .<sup>[5]</sup>

$$\sqrt{n} \left( \left( \frac{1}{n} \sum_{i=1}^n X_i \right) - \mu \right) \xrightarrow{d} \mathcal{N}(0, \sigma^2).$$

Convergence in distribution means that the **cumulative distribution function** of  $\sqrt{n}(S_n - \mu)$  converges pointwise to the cdf of the  $N(0, \sigma^2)$  distribution: for any real number  $z$ ,

$$\lim_{n \rightarrow \infty} \Pr[\sqrt{n}(S_n - \mu) \leq z] = \Phi(z/\sigma),$$

where  $\Phi(x)$  is the standard normal cdf.

# Density fluctuations

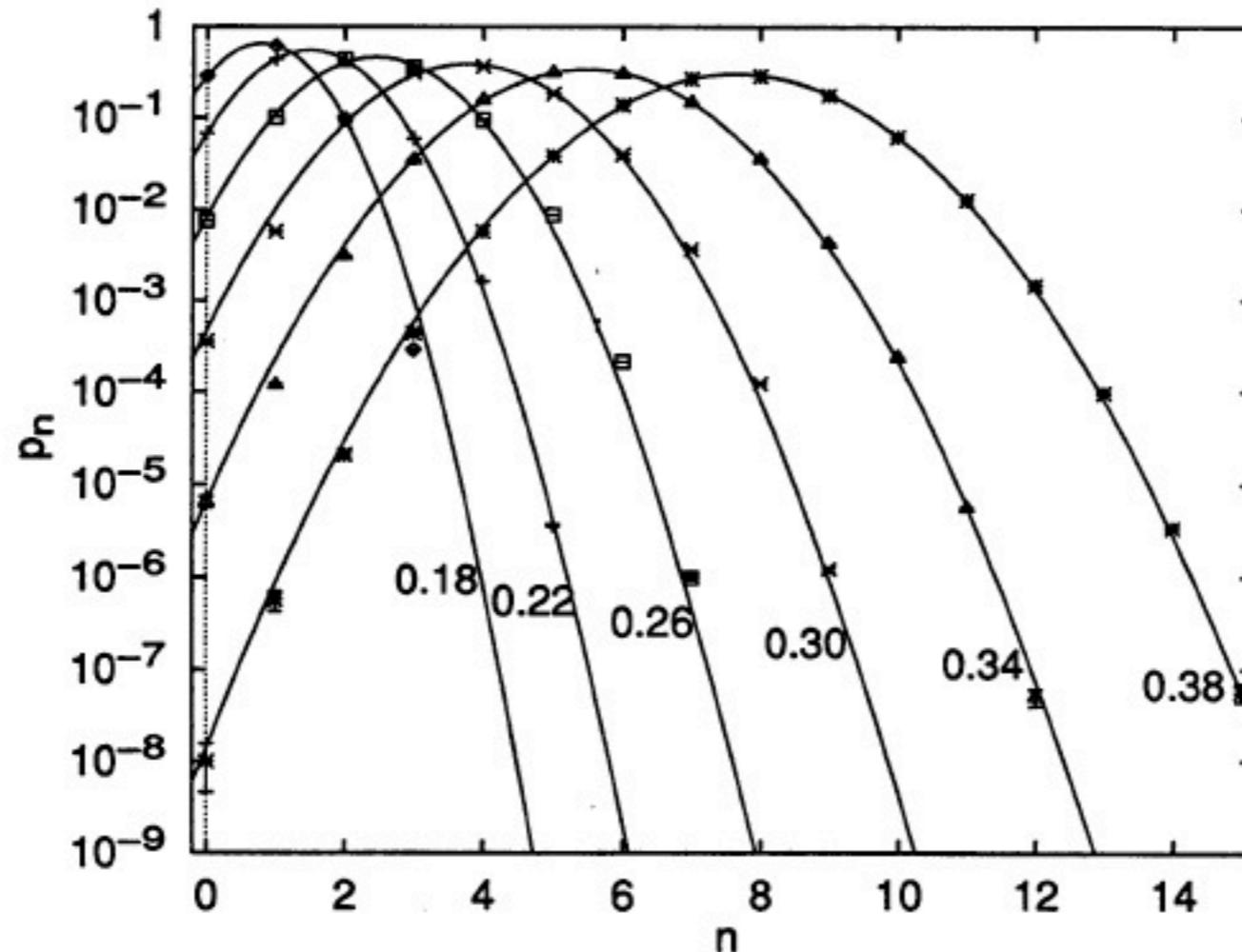


FIG. 1. Probabilities  $p_n$  of observing  $n$  solvent centers in spherical cavity volumes. Results from Monte Carlo simulation (57) of 512 SPC water molecules (58) are shown as symbols. The parabolas are the predictions of information theory using the flat default model and the moments of Eqs. 2 and 3. The center-to-center exclusion distance,  $d$  (in nanometers), is noted next to each curve.

An information theory model of hydrophobic interactions.  
G Hummer, S Garde, A E García, A Pohorille, and L R Pratt  
*Proc. Natl. Acad. Sci. USA* **93**, 8951 (1996)

# Gaussian potentials

## Classical electrostatic model

In the microscopic picture the free energy curve is a similar parabola as with the conducting spheres ( $a$  is a microscopic length).

$$\Delta G \sim \frac{1}{a} \cdot \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \cdot (\Delta e)^2$$

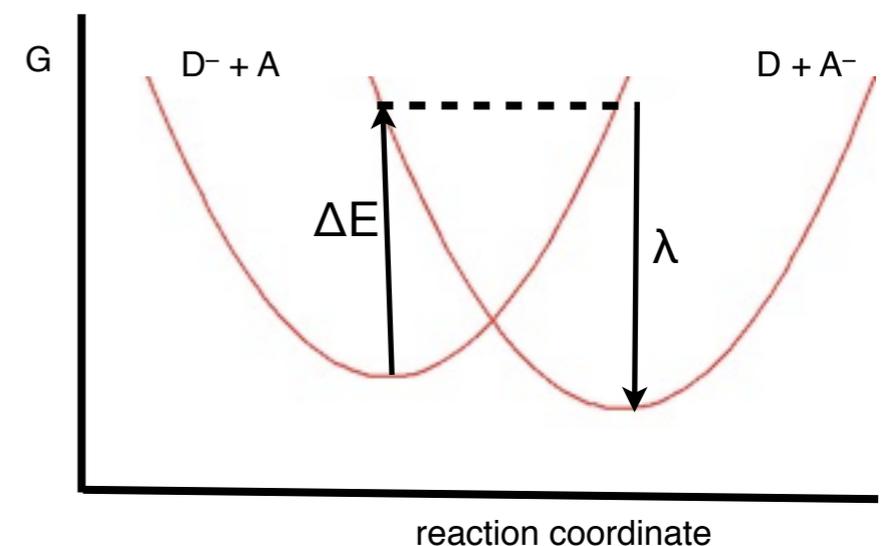
When moving one electron charge,  $\Delta G = \lambda - \Delta G_0$   
so that

$$\lambda \sim \frac{1}{a} \cdot \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \cdot e^2$$

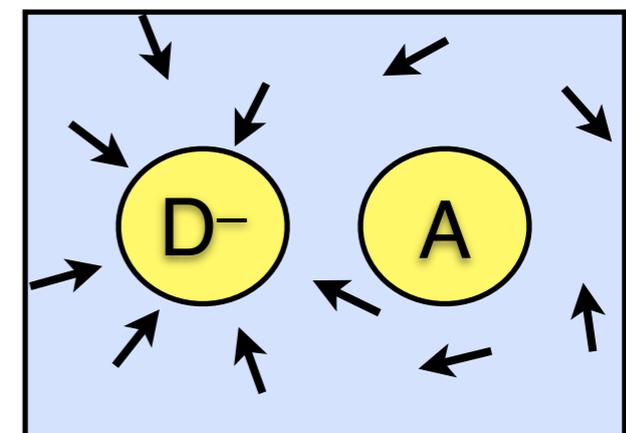
For water the static dielectric constant is about 80 and the optical constant about 2. This gives for the reorganization free energy a number close to 2 eV.

The reorganization free energy is not completely a universal property of the solvent. Also inner sphere reorganization (ligand fluctuation) plays a small part. Therefore, also in non-polar solvents  $\lambda$  is not zero. (Benzene gives 0.2-0.6 eV).

## diabatic



## Reactant state



# Inner sphere

## Classical electrostatic model

The reorganization free energy is not completely a universal property of the solvent. Also inner sphere reorganization (ligand fluctuation) plays a small part.

Inner sphere reorganization refers to vibrational changes inside the redox species (molecule or complex).

For the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple, the breathing modes of the 6 water molecules in the first coordination shell (ligands) change.

Assuming harmonic conditions and frequencies  $\nu_D$  and  $\nu_A$ , the force constants,  $f_D$  and  $f_A$  are:  $f = 4\pi^2\nu^2\mu$  and the energies are:

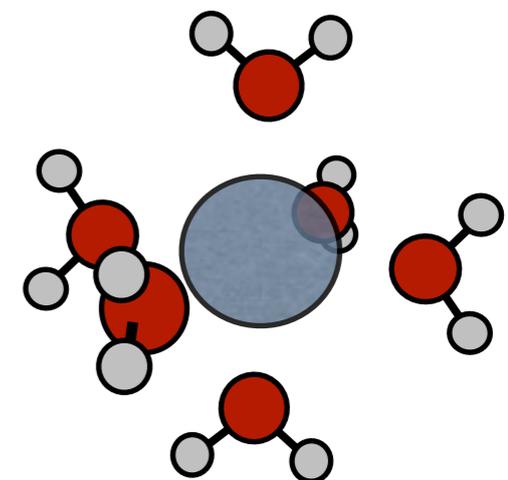
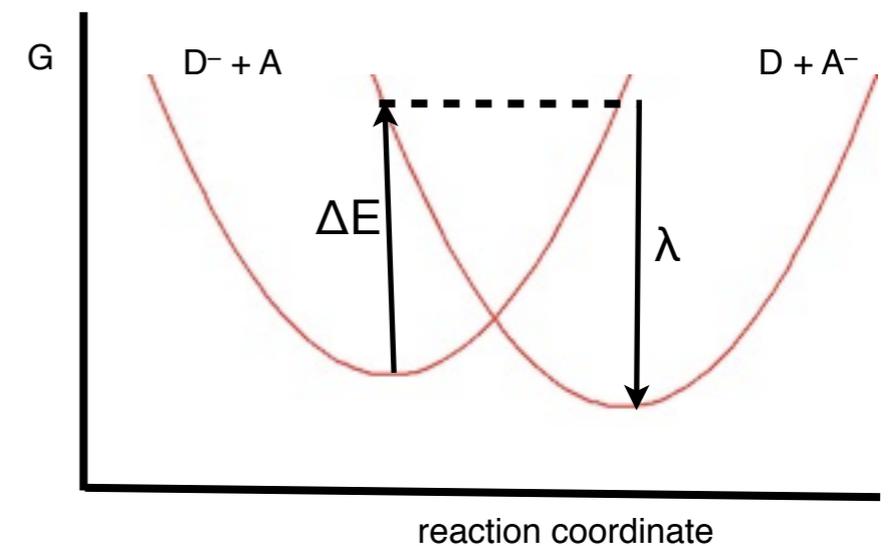
$$E_D = E_D(q_0, D) + 3f_D(\Delta q_D)^2$$

$$E_A = E_A(q_0, A) + 3f_A(\Delta q_A)^2$$

Also in the inner sphere reorganization the potential energy curve is quadratic, but here it is due to the vibrations.

$$q^* = \frac{q_{0,D}f_D + q_{0,A}f_A}{f_D + f_A} \quad \lambda_{in} = \Delta E^* = \frac{3f_Df_A}{f_D + f_A}(q_{0,D} - q_{0,A})^2$$

diabatic

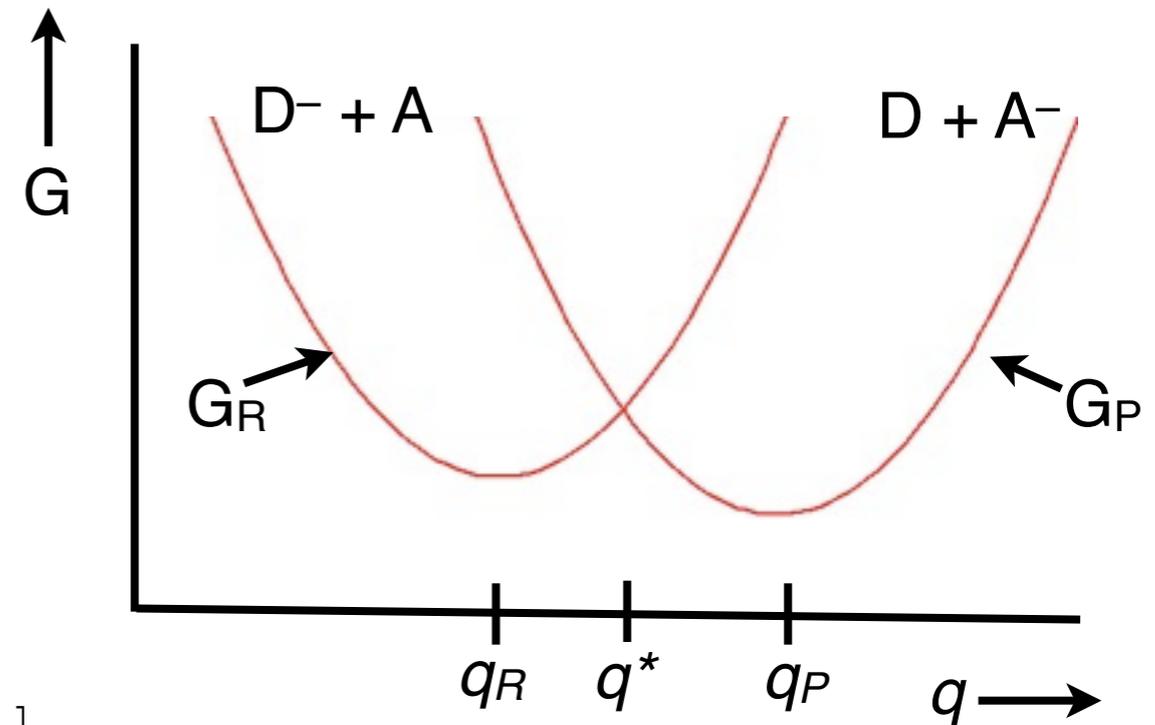


# Energy barrier

## Gaussian potential curves

$$G_R = G_R^0 + \frac{1}{2}k(q - q_R)^2$$

$$G_P = G_P^0 + \frac{1}{2}k(q - q_P)^2$$



## Where do they cross?

$$G_P^0 - G_R^0 = \frac{k}{2}[q^2 - 2q_Pq + q_P^2 - q^2 + 2q_Rq - q_R^2]$$

$$2\frac{(G_P^0 - G_R^0)}{k} = 2(q_R - q_P)q + q_P^2 - q_R^2$$

$$q^* = \frac{1}{2}(q_R^2 - q_P^2) + \frac{\Delta G_0}{k(q_R - q_P)}$$

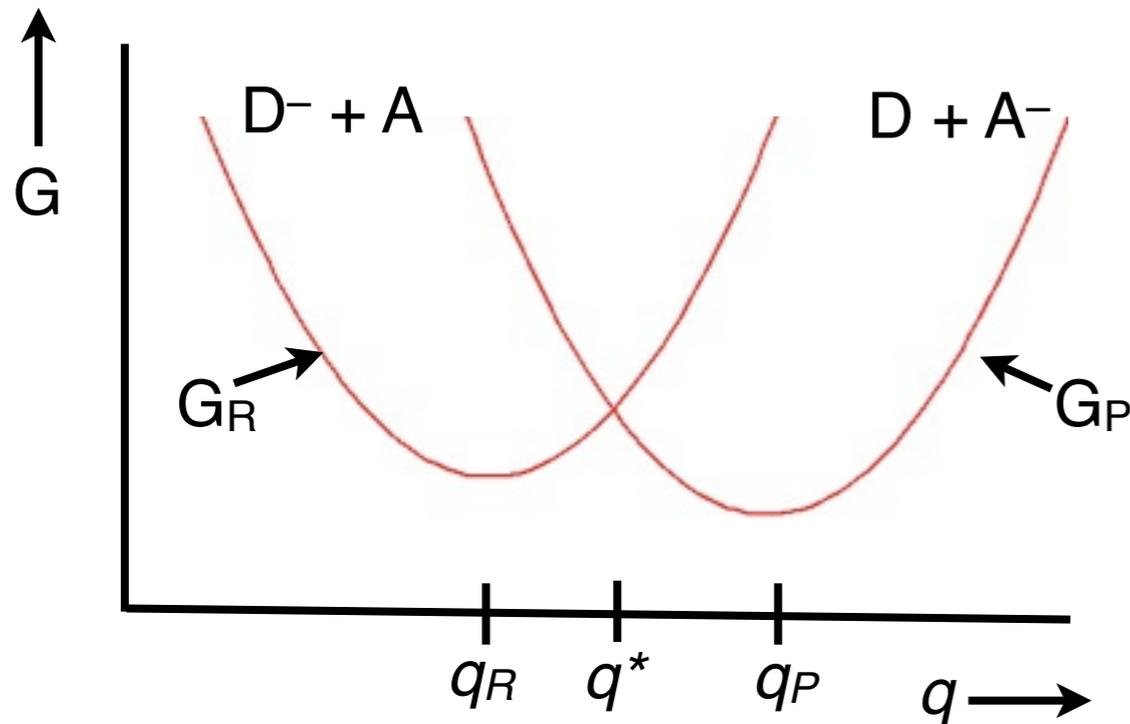
$$\Delta G^* = \frac{1}{2}k\left[\frac{1}{2}(q_R^2 - q_P^2) + \frac{\Delta G_0}{k(q_R - q_P)}\right]^2$$

## With reorganization free energy, $\lambda$

$$\lambda = \frac{1}{2}k(q_P - q_R)^2$$

$$\Delta G^* = \frac{(\lambda + \Delta G_0)^2}{4\lambda}$$

# Fermi's golden rule



$$p_{i \rightarrow j} = \frac{2\pi}{\hbar} |\langle \psi_i | V | \psi_j \rangle|^2 \rho_j$$

The probability of a transition from an eigenstate  $|\psi_i\rangle$  to a final state  $|\psi_j\rangle$  depends on the overlap between the states and the degeneracy (density,  $\rho$ ) of the final state.

Fermi's golden rule was first derived by Dirac, using time-dependent perturbation theory to first order, using a (time-dependent) perturbation interaction,  $V$ .

## The transfer barrier

$$\Delta G^* = \frac{(\lambda + \Delta G_0)^2}{4\lambda} \quad \lambda = \frac{1}{2}k(q_P - q_R)^2$$

## The rate

The electron transfer rate is the obtained using the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}\right)$$

## Total non-adiabatic solution

$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}\right)$$

# Marcus inverted region

## The transfer barrier

The electron transfer rate is the obtained using the Arrhenius equation:

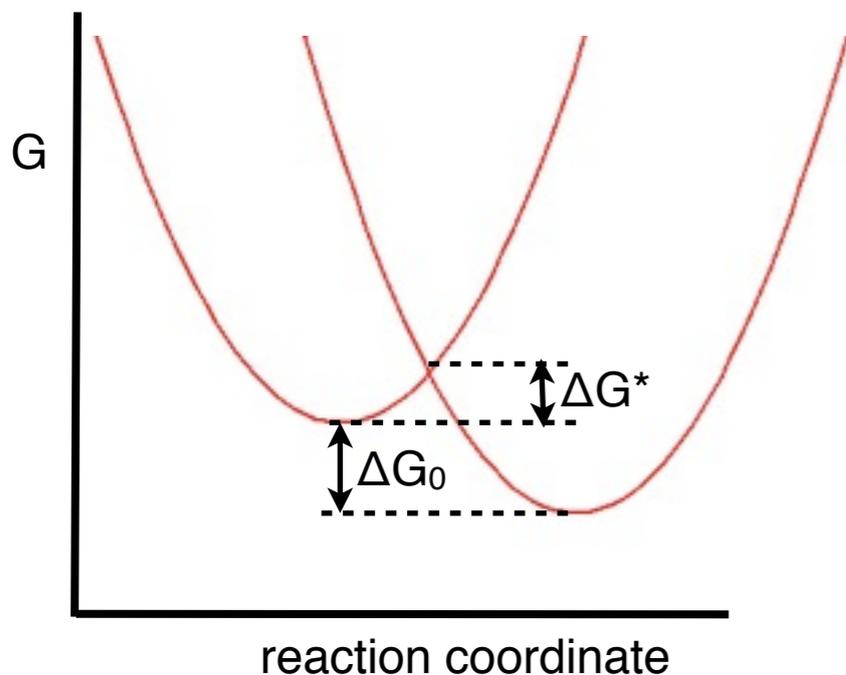
$$\Delta G^* = \frac{(\lambda + \Delta G_0)^2}{4\lambda}$$

$$\lambda = \frac{1}{2}k(q_P - q_R)^2$$

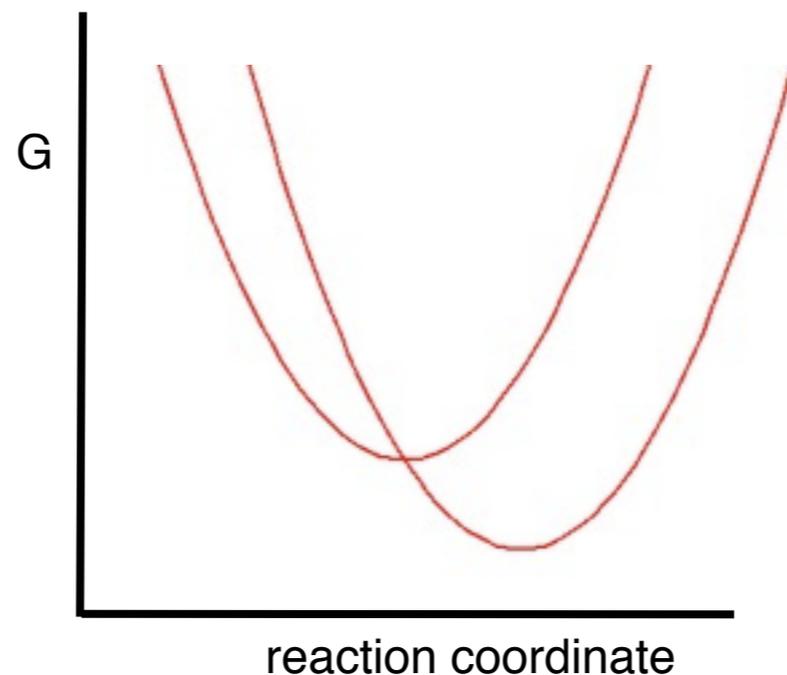
$$k = k_0 \exp\left(-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}\right)$$

$$\Delta G_0 = \Delta E + \lambda$$

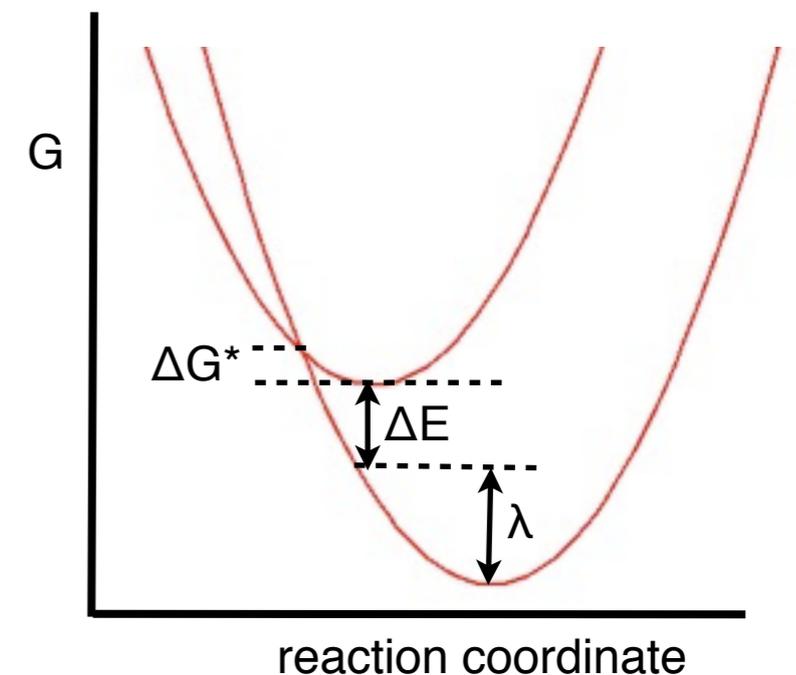
Increasing of the “driving force”  $\Delta G_0$  increases the rate (as expected)



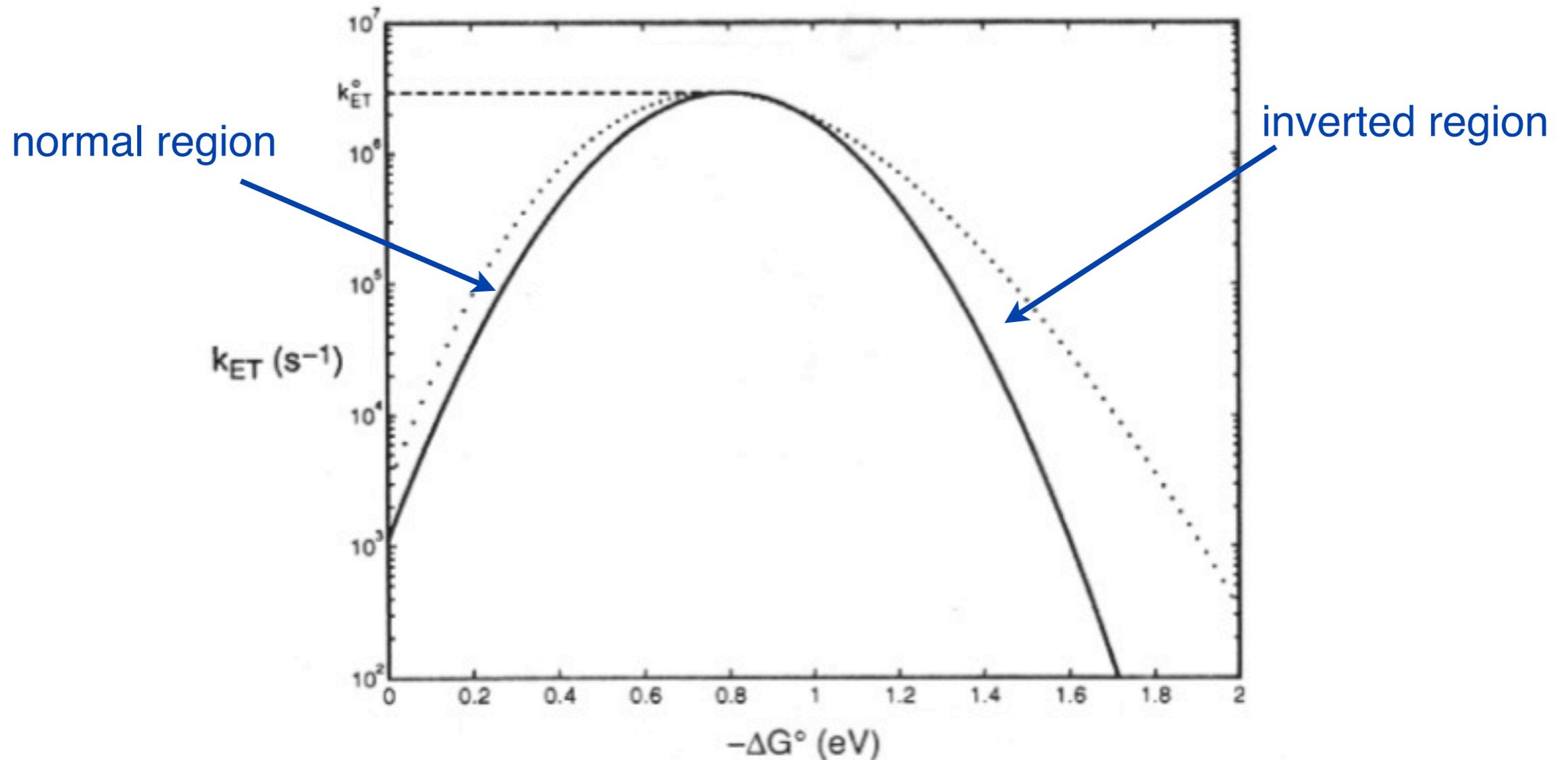
No barrier;  $\Delta G^* = 0$ ,  
 $\Delta G_0 = \lambda$



Inverted region: barrier increases with  $\Delta G_0$  (rate decreases)



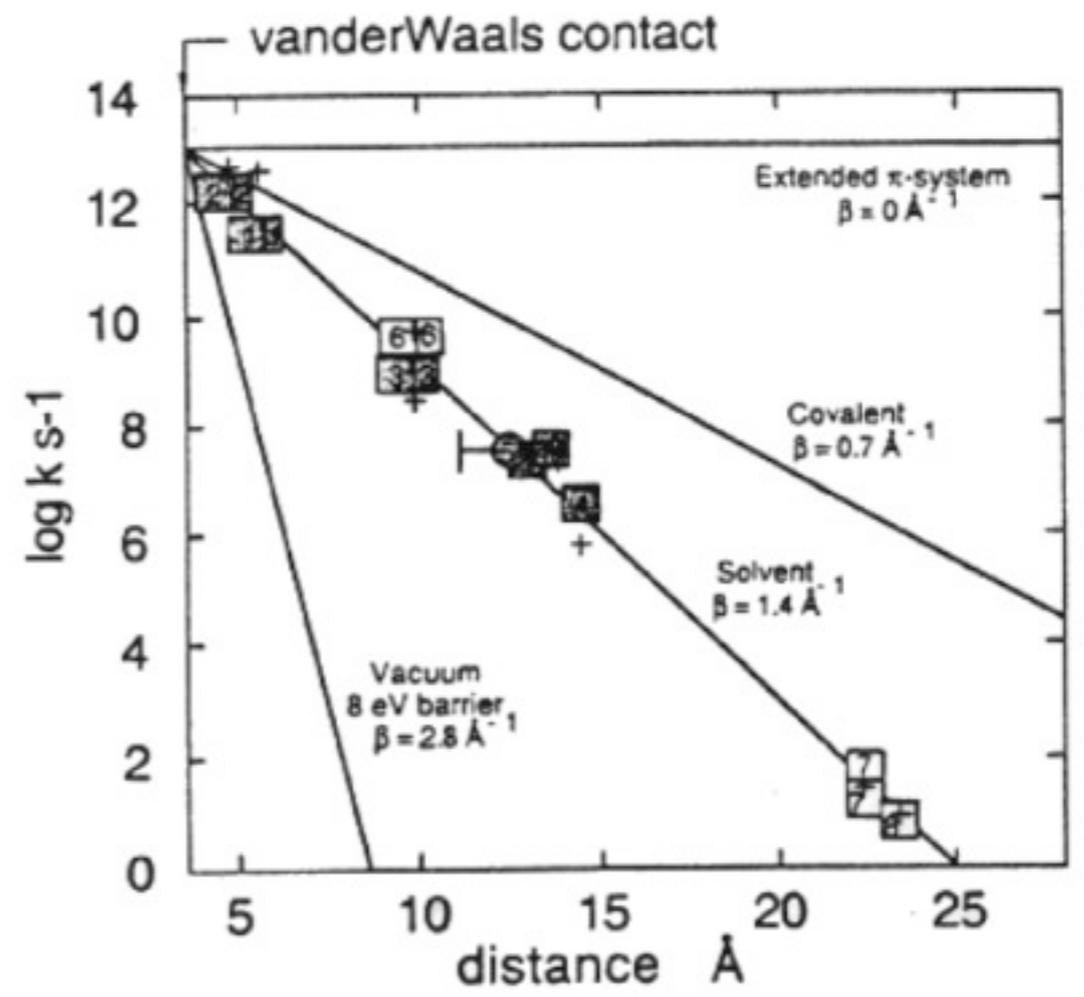
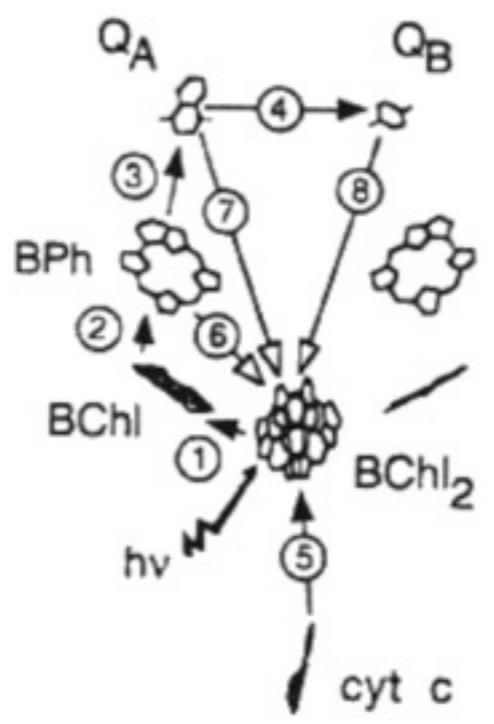
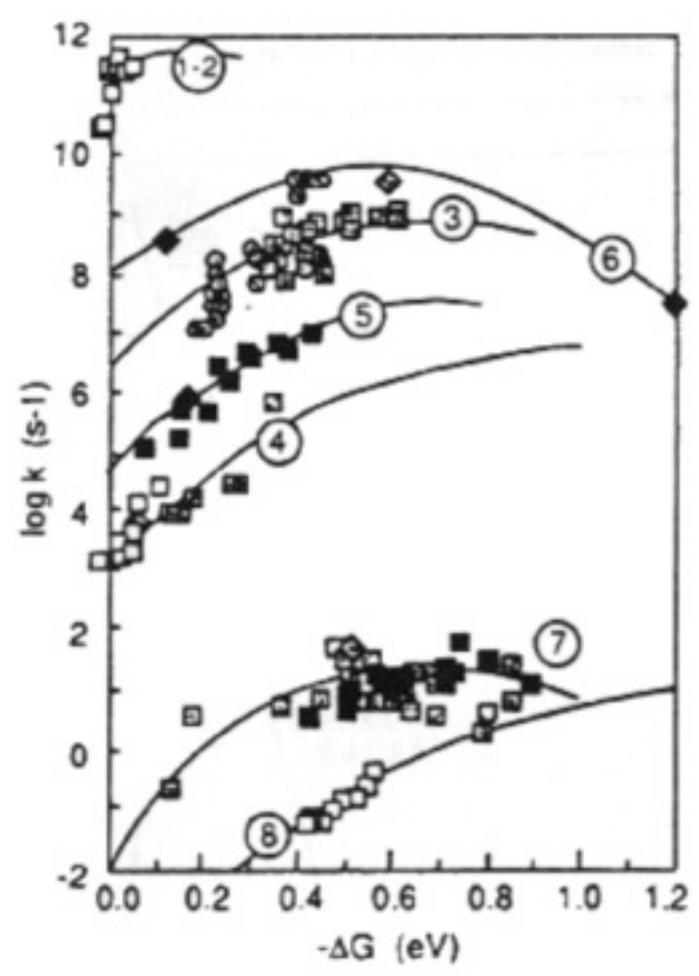
# Marcus inverted region



- Marcus published his theory in JCP 1956
- Experiments with reactions of increasing  $\Delta G_0$  show increasing rate (up to diffusion limit)
- Until Miller, Calcaterra, Closs, JACS 106, 3047 (1984), inverted region in intermolecular ET, with donor and acceptor at fixed distance

# Dutton's ruler

- Comparison of different  $\Delta G_0$  in photosynthetic reaction center by
- regarding different electron transfer processes (different D-A distance)
  - replacing donor or acceptor amino acids (environment remains unchanged)



$$\log_{10} k_{et} = 13 - 0.6(R - 3.6) - 3.1(\Delta G_0 + \lambda)^2 / \lambda$$

# Summary

- Marcus theory builds on Arrhenius equation
- Formula for the rate
- Dependence of activation energy on driving force  $\Delta G_0$  and reorganization free energy
- Environment response by inner and outer sphere reorganization
- Gaussian potential functions (linear response of environment)
- Inverted region when  $\lambda < \Delta G_0$

# Electron transfer

## quantum mechanical picture

Consider two identical ions, A and B, separated by a distance  $R$  and an extra electron.

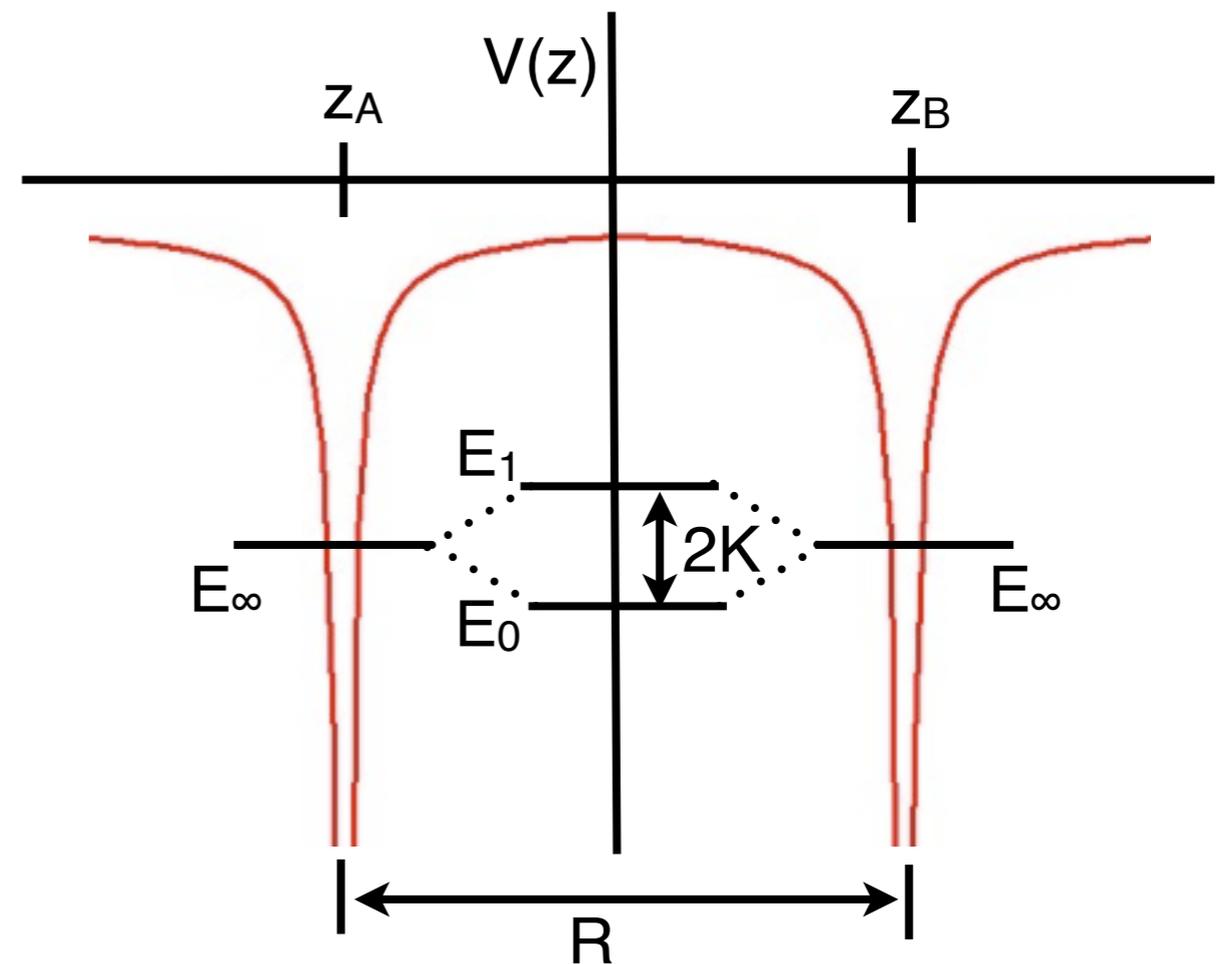
For very large  $R$ , the electron sits either on A or B, and the degenerate states  $|A\rangle$  and  $|B\rangle$  do not mix.

For a typical ion-contact pair distance ( $\sim 5 \text{ \AA}$ ), the two states are coupled, resulting into two mixed states,  $E = E_\infty \pm K$ , with a gap of  $2K$ .

$$\langle A|H_0|B \rangle = -K$$

$$H_0 = \begin{bmatrix} 0 & -K \\ -K & 0 \end{bmatrix}$$

- $K$  decays exponentially with distance
- The coupling is small but not zero (otherwise there would be no transfer)
- An asymmetric redox pair tilts the picture
- Adding a solvent will increase the gap and the asymmetry.



# Electron transfer

## quantum mechanical picture

Adding ligands and solvent changes the Hamiltonian.

If the electron is mainly localized on one of the two ions, the gap is increased by the solvent reaction field that interacts with the redox pair dipole. The solvation energy is:

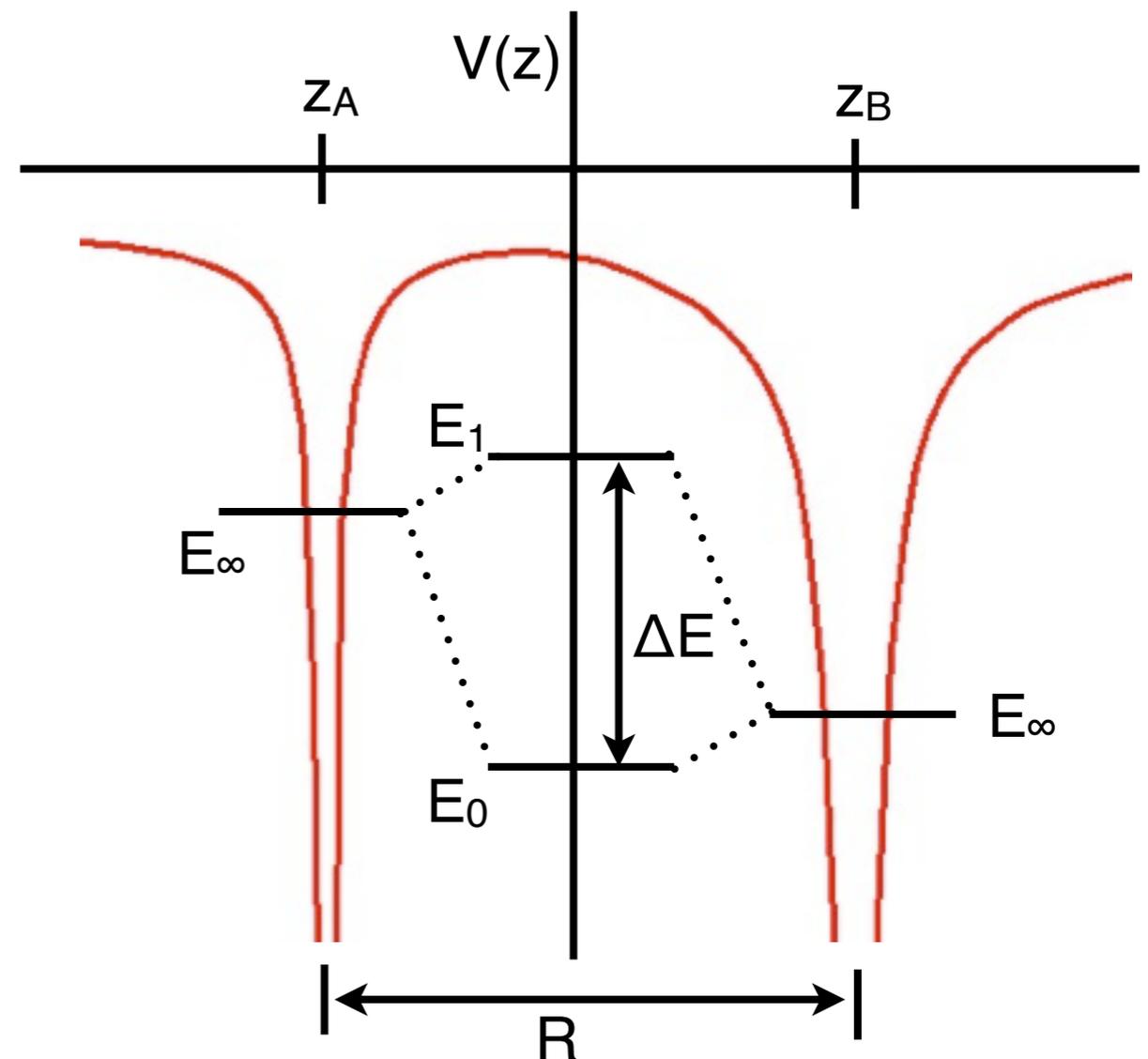
$$E_{\text{solv}} \approx -\frac{e^2}{a} \left(1 - \frac{1}{\epsilon_s}\right)$$

If the electron is delocalized over the two ions, the dipole fluctuations are too fast to couple to the solvent configuration; only the electronic polarizability couples. The solvation energy is:

$$E_{\text{solv}} \approx -\frac{e^2}{a} \left(1 - \frac{1}{\epsilon_{\text{opt}}}\right)$$

Thus:

$$\Delta E \sim \frac{e^2}{a} \cdot \left(\frac{1}{\epsilon_{\text{opt}}} - \frac{1}{\epsilon_s}\right) \approx \frac{e^2}{a\epsilon_{\text{opt}}}$$



# Electron transfer

## quantum mechanical picture

The total Hamiltonian is:

$$H = \begin{bmatrix} 0 & -K \\ -K & -\Delta e \end{bmatrix} - \mathcal{E} \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} + H_{bath}(x_1, x_2, \dots, x_N) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} H_A & -K \\ -K & H_B \end{bmatrix}$$

$\mathcal{E}$  is the local electric field on the redox dipole.  
It shows Gaussian statistics. (inner shell / outer shell)

The environment contributes  $2\mathcal{E}$  to the gap:

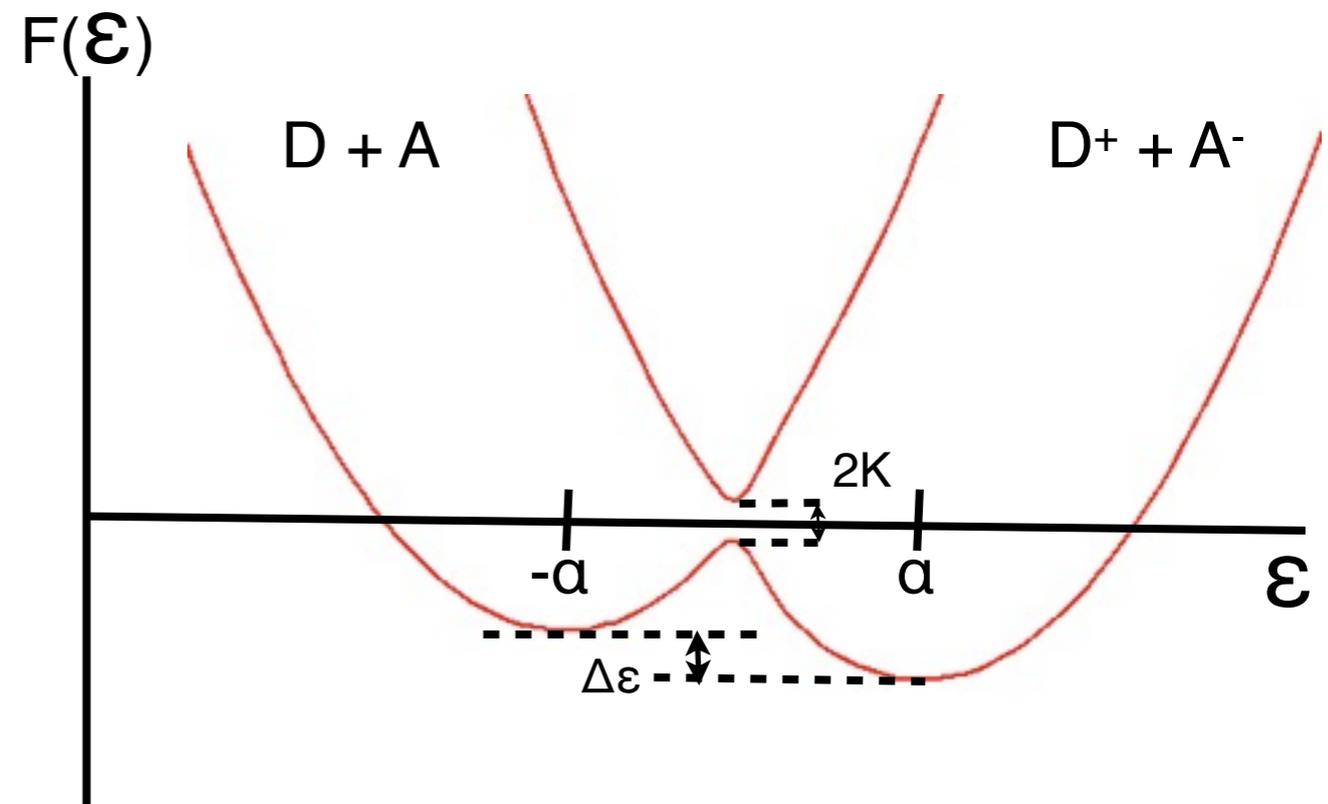
$$\Delta E = H_B - H_A = -\Delta\epsilon - 2\mathcal{E}$$

$H_X$  is total Hamiltonian when electron is on site  $X$ .

$$F_b(\mathcal{E}) = \frac{1}{2\alpha} \mathcal{E}^2$$

$$\langle \mathcal{E} \rangle_b = 0 \quad \langle \mathcal{E}^2 \rangle_b = k_B T \alpha$$

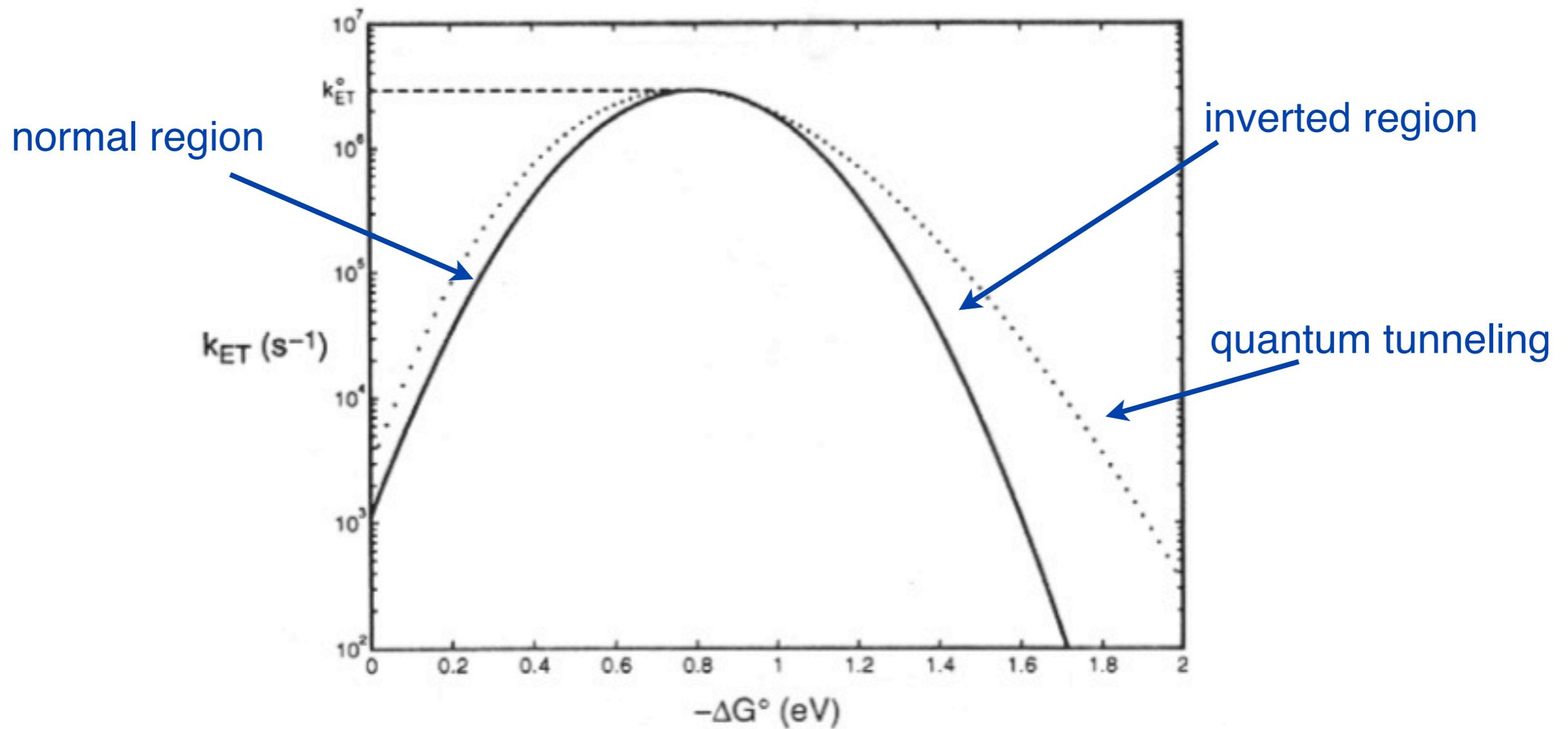
$$F_A(\mathcal{E}) = \frac{1}{2\alpha} \mathcal{E}^2 + \mathcal{E} \quad F_B(\mathcal{E}) = \frac{1}{2\alpha} \mathcal{E}^2 - \mathcal{E} - \Delta\epsilon$$



adiabatic

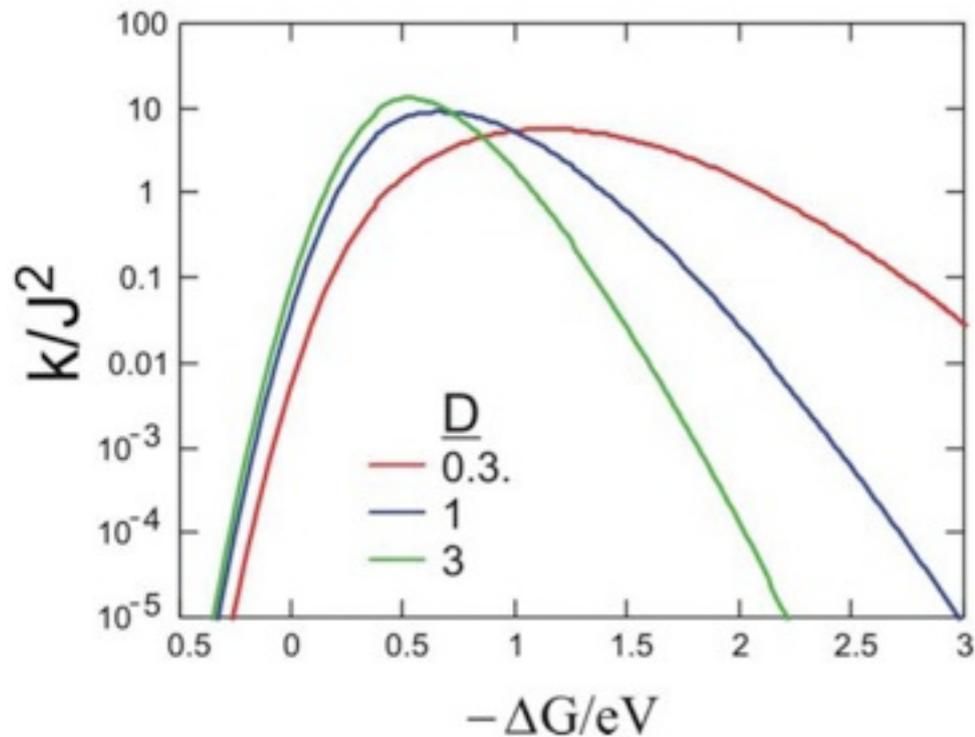
spin boson model

# Marcus inverted region



# Quantum effects

Vibrational frequency:  $\omega_0 := 2000 \text{ cm}^{-1}$   
 Solvent reorganization energy:  $\lambda_0 := 0.5 \text{ eV}$



## Spectral density of gap correlation

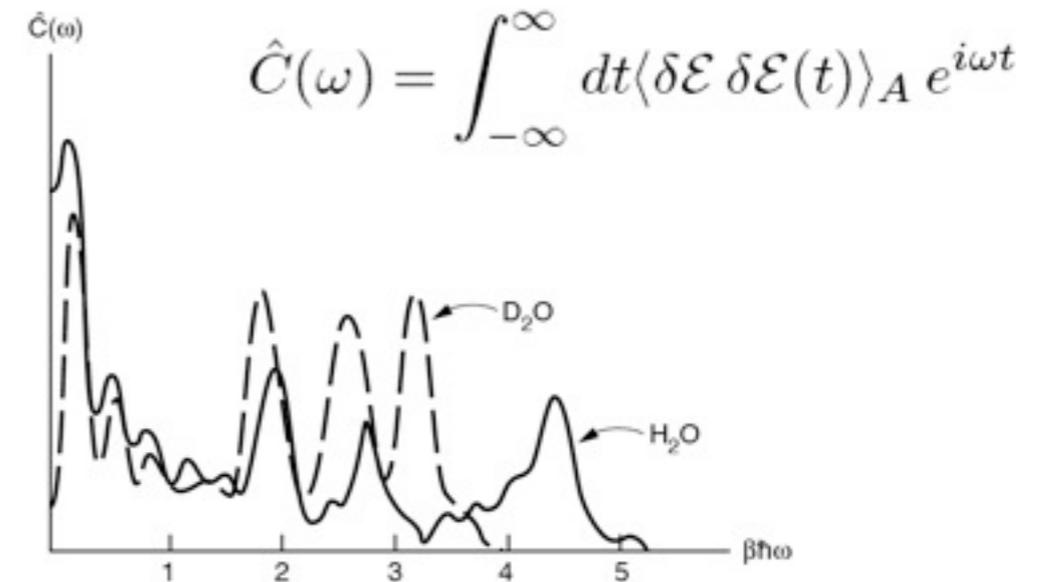


Fig. 10. - Fourier transform of the energy gap correlation function computed from classical computer simulation trajectories of the ferrous-ferric pair in water, and deuterated water.

$$k_{A \rightarrow B} \approx \frac{2\pi}{\hbar} K^2 \left| \frac{\theta^3(t^*)}{2\pi\hbar\theta''(t^*)} \right|^{1/2},$$

$$\theta(t) = \exp \left\{ -\frac{1}{4\pi\hbar} \int_0^\infty d\omega \beta \hat{C}(\omega) \left[ \cosh(\beta\hbar\omega/2) - \cosh\left(\frac{\beta\hbar\omega}{2} - \omega t\right) \right] / \omega \sinh\left(\frac{\beta\hbar\omega}{2}\right) \right\} \exp(-\Delta\epsilon t/\hbar)$$

quantum nature of water for  $\text{Fe}^{3+}/\text{Fe}^{2+}$

$$k_{ET}/k_{ET}^{\text{classical}} \approx 60, \quad \text{H}_2\text{O}$$

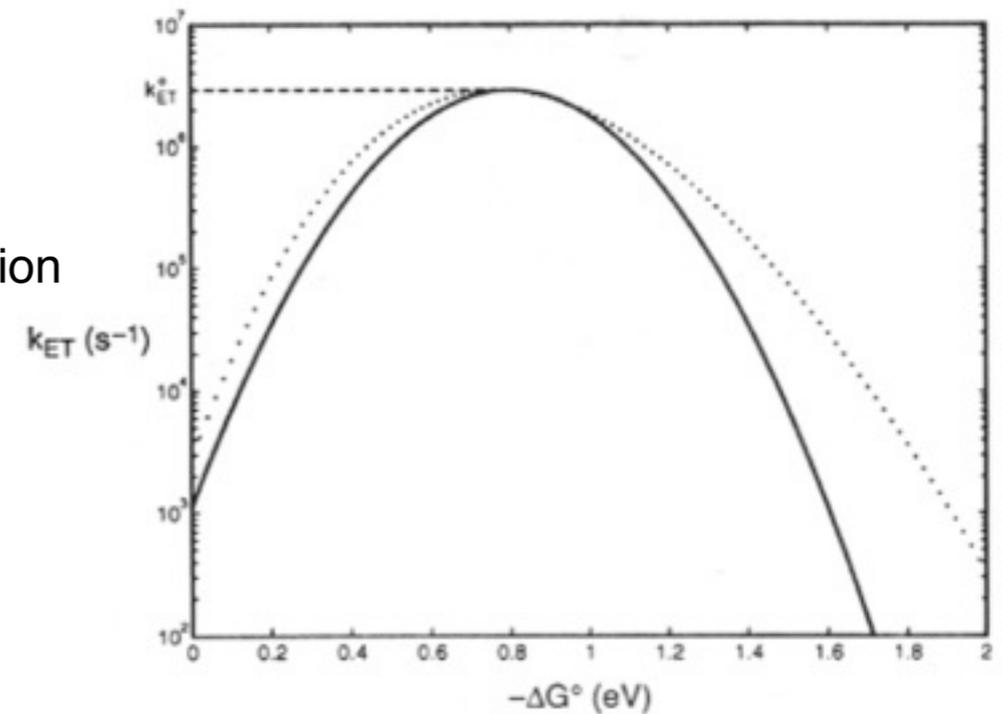
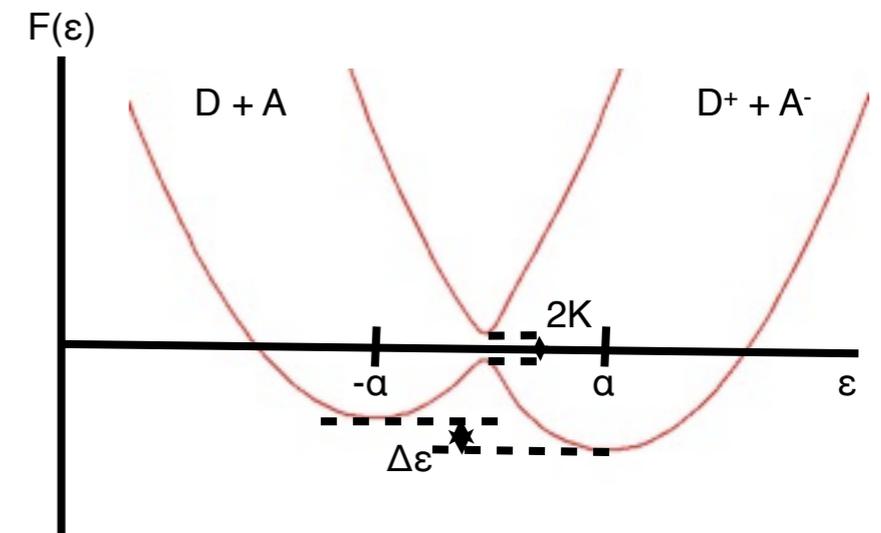
$$\approx 25, \quad \text{D}_2\text{O}$$

# Summary Part 1

## Marcus theory of Electron transfer

$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{2}{\sqrt{4\pi\lambda k_B T}} \exp - \frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}$$

1. reaction rate theory (Eyring) or vibronic excitation (Franck-Condon)
2. Gaussian potentials when polarization is the reaction coordinate
3.  $\lambda$  = inner sphere (harmonic vibrations) plus outer sphere (central limit theory) reorganization
4. dependence of activation energy on driving force  $\Delta G_0$  and reorganization free energy
5. inverted region when  $\lambda < \Delta G_0$
6. adiabatic vs diabatic picture (energy gap versus Fermi's golden rule)
7. quantum tunneling



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