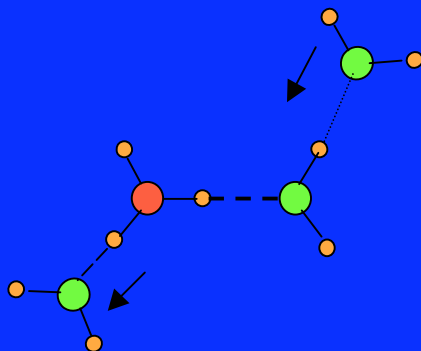


# THEORETICAL MODELS FOR PROTON TRANSFER IN CONDENSED MEDIA



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# Overview

Introduction

PT between a donor and an acceptor in polar media

PT in the hydrogen bonded systems, water

Comment on the relationship with MDS

Surface conductivity

Summary

# Introduction

Two main problems in proton transfer.

1. Proton transport from one region of the medium to another :  
macroscopic equations (diffusion coefficient, mobility)
2. Elucidation of the transfer mechanism and  
calculation of kinetic coefficients (diffusion coefficient, mobility):  
microscopic problem related with the calculation of the probabilities  
of proton jumps

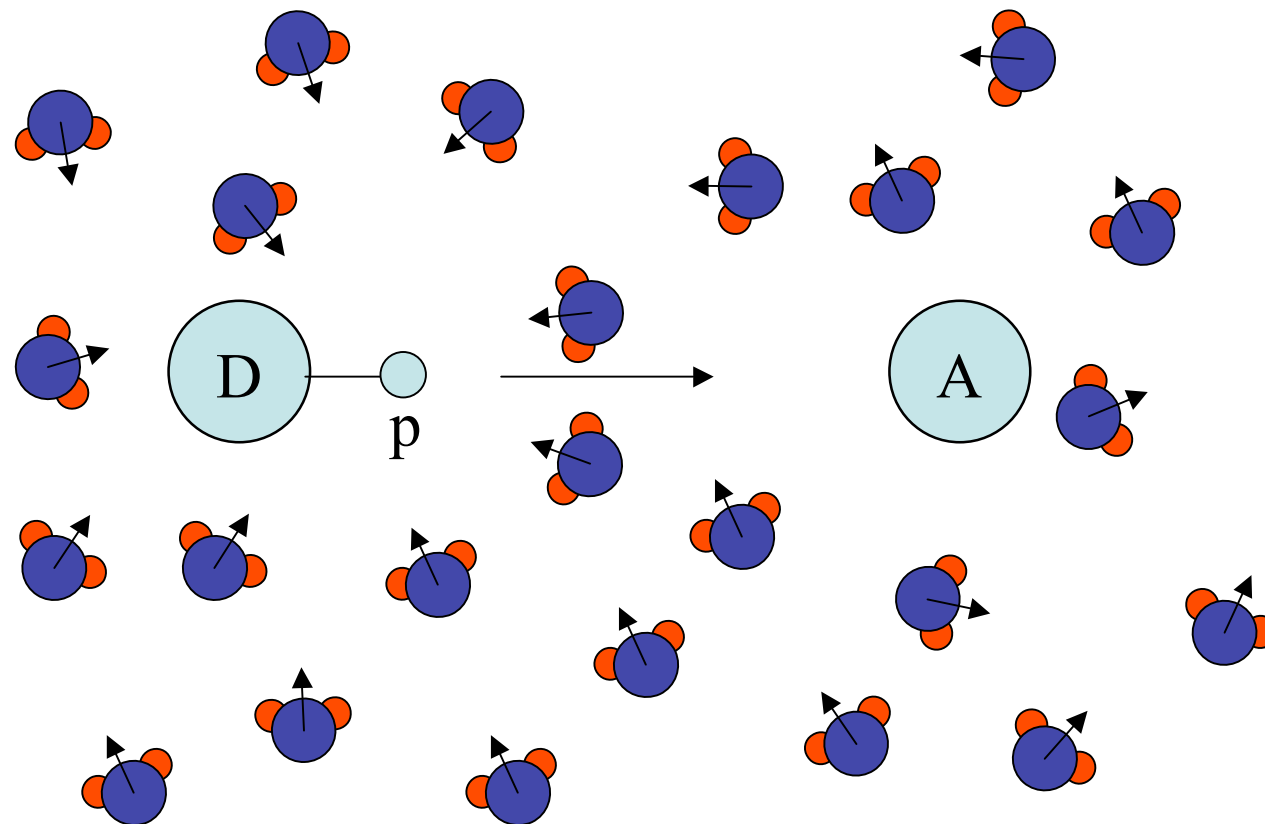
The second problem will be discussed.

First theories: R.P.Bell, St.Christov (weak interaction with the medium,  
only proton motion in a potential)

Strong coupling with the medium (R.R.Dogonadze, A.M.Kuznetsov et al.,  
J.T.Hynes et al., L.I.Trakhtenberg et al.,  
Sh.Hammes-Schiffer et al., G.A.Voth et al.,  
A.Warshel et al., D.Truhlar et al. ....)

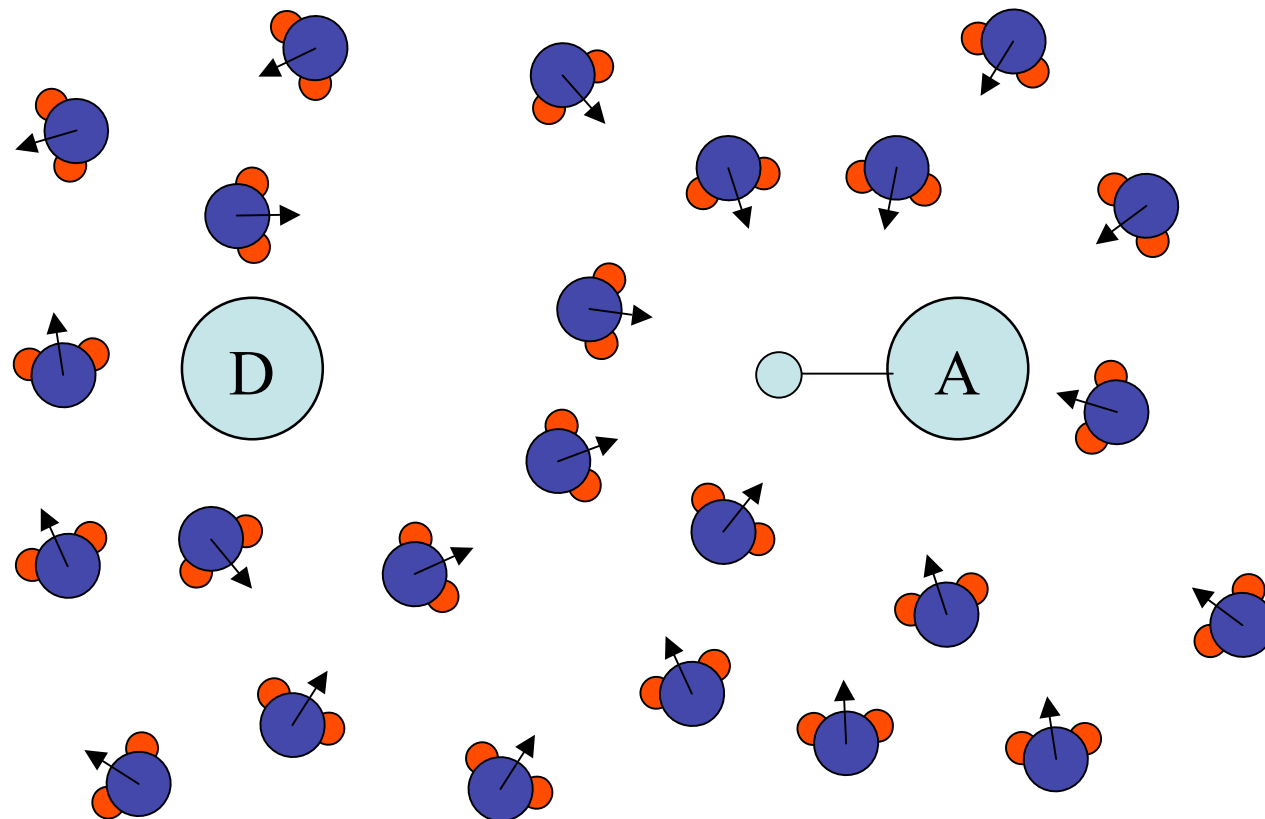
# Proton transfer between two sites (species) in a polar medium (i)

i



# Proton transfer between two sites (species) in a polar medium (f)

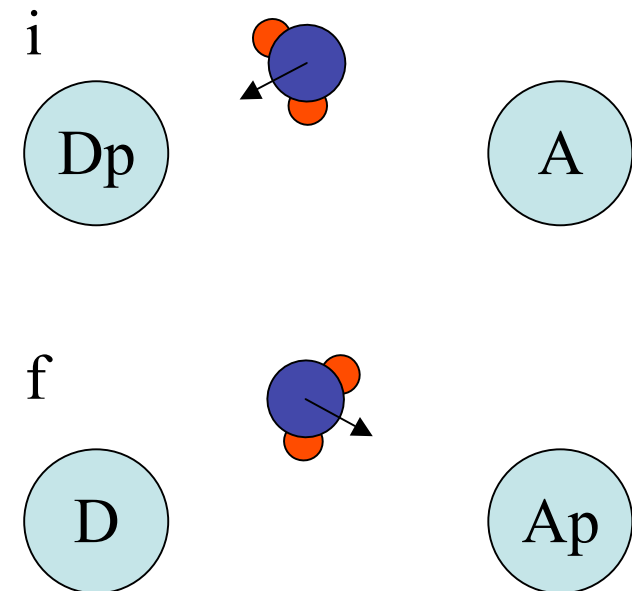
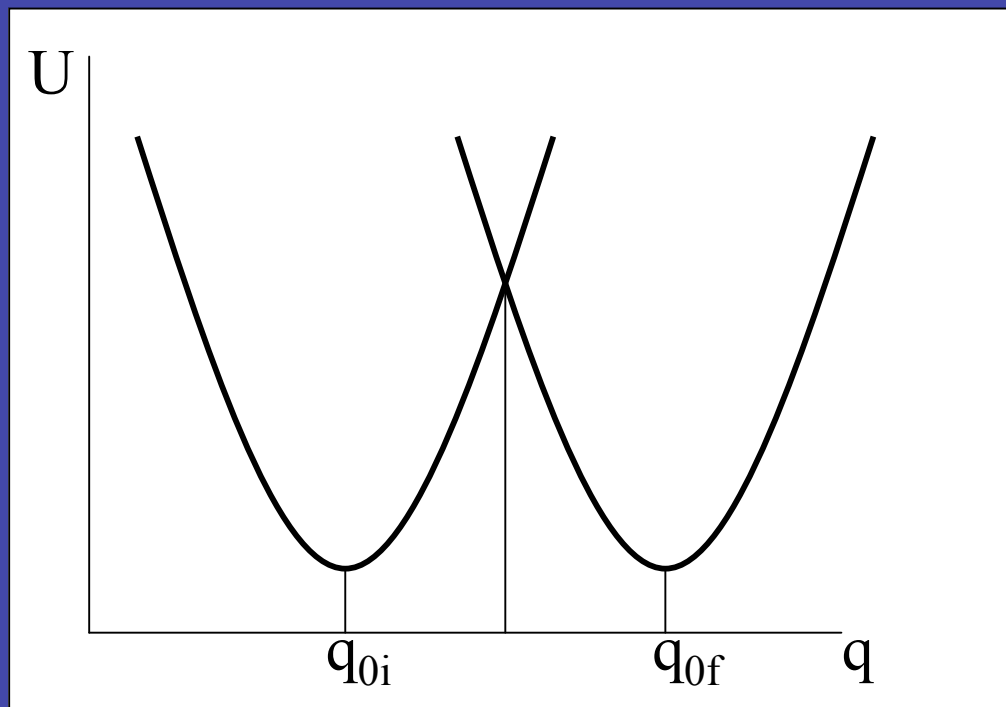
f



# Reactive modes

Points of importance:

1. Proton **strongly interacts** with the medium polarization and in general with some local vibrational modes
2. All these degrees of freedom constitute **REACTIVE MODES**
3. **Equilibrium configurations** of reactive modes depend on the **proton localization**



# Classical and quantum degrees of freedom

Classical modes: most of vibrational degrees of freedom in the molecular environment (solvent polarization, intermolecular vibrations, soft local modes)

Quantum subsystem: electrons, proton, some high-frequency vibrational modes

Proton is a quantum particle:(a) discrete vibrational energy levels,  
vibrational energy quantum is larger  
than

thermal energy

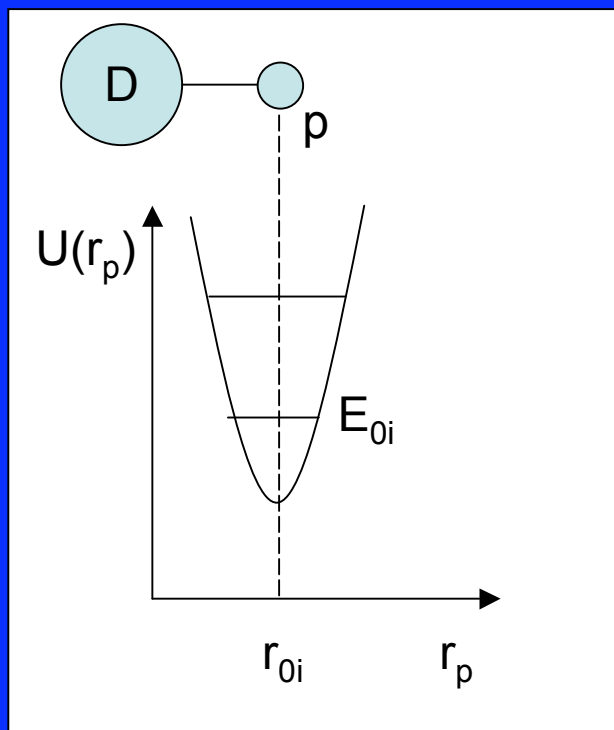
$$\Omega > k_B T$$

(b) tunneling

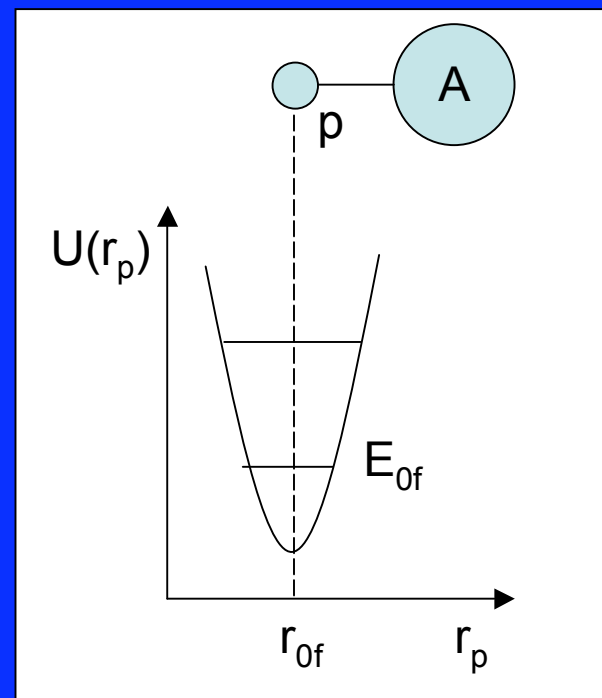
# Totally nonadiabatic transitions

Electronically nonadiabatic transitions (R.R.Dogonadze, A.M.Kuznetsov, V.G.Levich, 1967-1970 )

Initial state



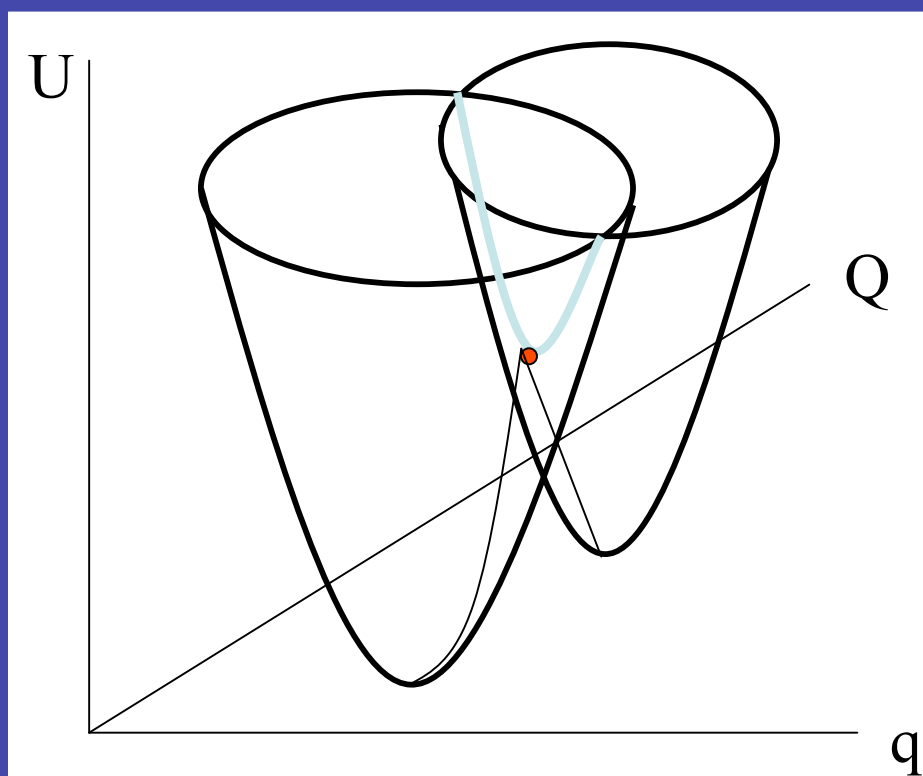
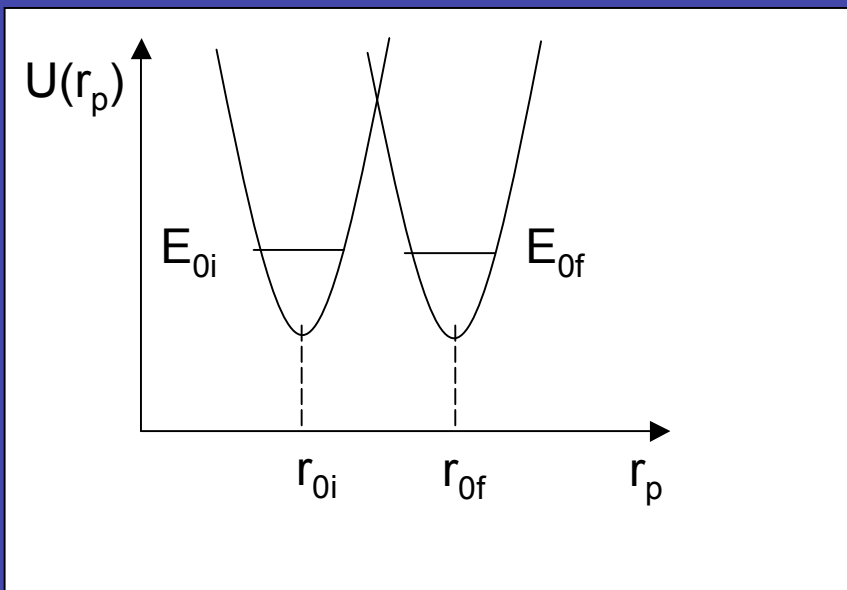
Final state



Discrete vibrational energy levels with a separation  $\gg k_B T$



# A generalized Franck – Condon principle



- Saddle point corresponds to minimum free energy and determines the activation free energy

# Activation free energy and pre-exponential factor

$$W = \langle \varphi_i | V_{\text{int.}} | \varphi_f \rangle^2 \sqrt{\frac{\pi}{\hbar^2 E_r k_B T}} e^{-\sigma} e^{-\frac{[E_r + \Delta F]^2}{4E_r k_B T}}$$

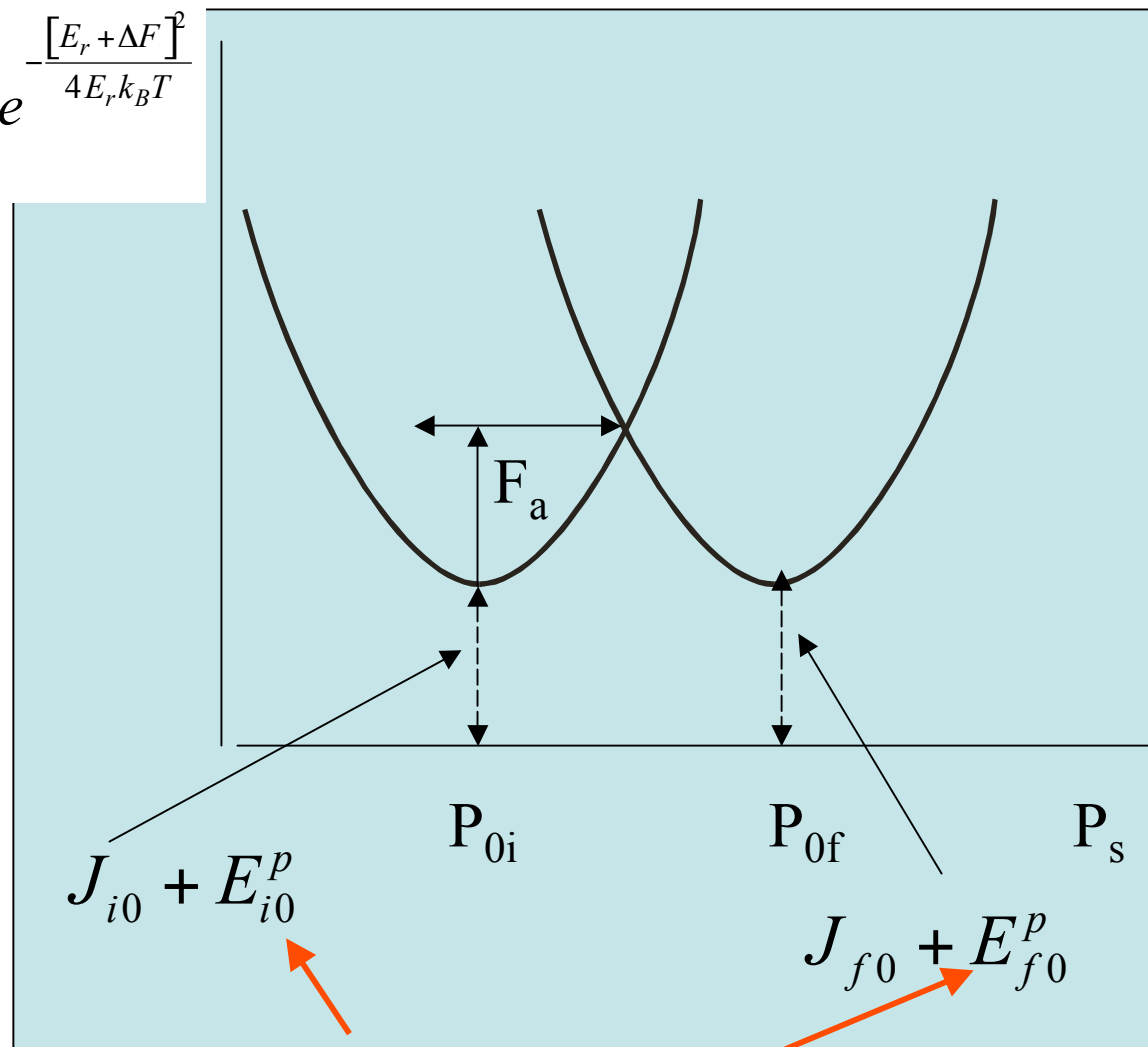
$$F_a = U_0^r(q^*) - U_0^r(q_{0i})$$

$$F_a = [E_r + \Delta F]^2 / 4E_r$$

$E_r$  is the reorganization energy of the solvent polarization and other classical modes

$$\Delta F = J_{f0} - J_{i0} + E_{f0}^p - E_{i0}^p$$

$$\sigma = \frac{E_r^p}{\hbar\Omega} = \frac{1}{2} \frac{m_p \Omega}{\hbar} (r_{oi} - r_{of})^2$$



Zero-point energies

# Criteria

Characteristic electron time  $\tau_{e(p)}$   
Characteristic proton times,  $\tau_{p(e)}$ ,  $\tau_{p(s)}$   
Characteristic "solvent" time  $\tau_s$

Totally nonadiabatic transitions:  $\tau_{e(p)} \gg \tau_{p(e)}$

$$\tau_{p(s)} \gg \tau_s$$

$$\tau_{e(p)} = \hbar / V_e$$

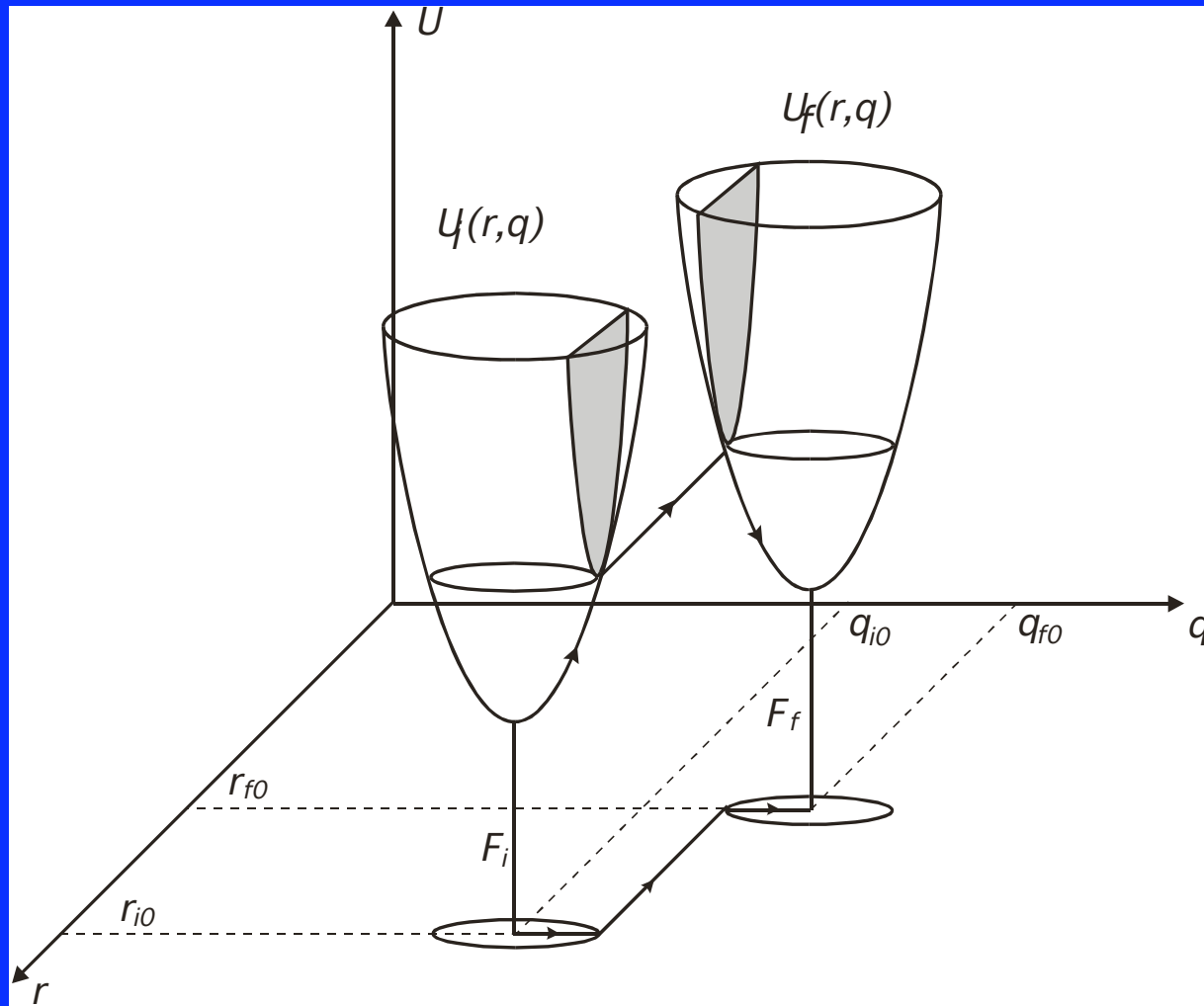
$$\tau_{p(e)} = \hbar V_e / |v_p| |F_{pi} - F_{pf}|$$

$$\tau_{p(s)} = \hbar / \Delta E$$

$$\tau_s = \hbar \Delta E / |v_s| |F_{si} - F_{sf}|$$



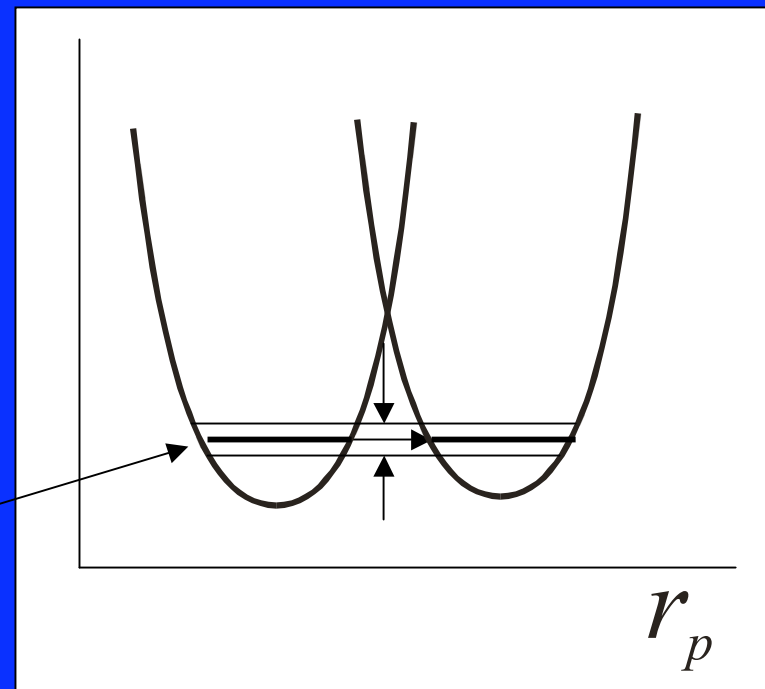
# Physical mechanism of the transition



## Pre-exponential factor

$$W = \left\langle \varphi_i \left| V_{\text{int.}} \right| \varphi_f \right\rangle^2 \sqrt{\frac{\pi}{\hbar^2 E_r k_B T}} e^{-\sigma} e^{-\frac{[E_r + \Delta F]^2}{4E_r k_B T}}$$

Resonance splitting of the proton energy levels



$$\Delta E \approx 2V_{ep} \approx 2V_{if} \left\langle \chi_{i0}^p \left| \chi_{f0}^p \right. \right\rangle = 2V_{if} e^{-\sigma_{00}/2}$$

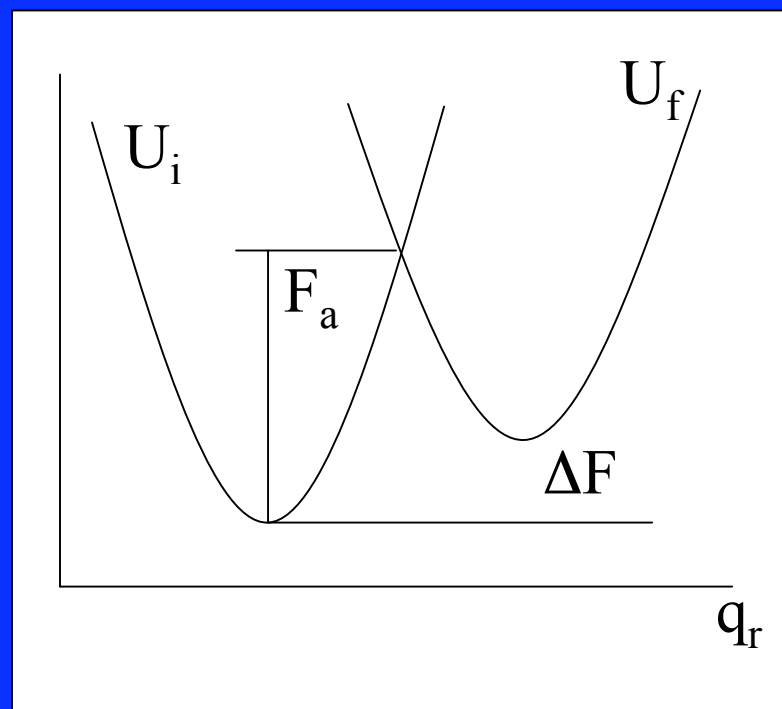
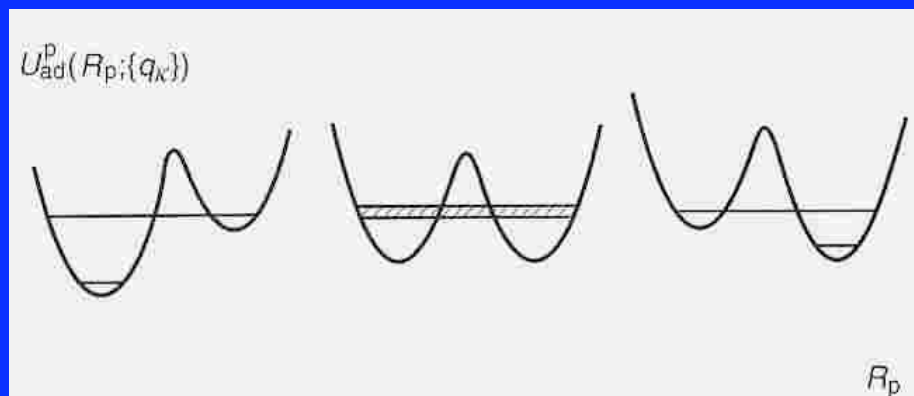
Activation free energy and pre-exponential factor are determined by potential barriers along different coordinates:  $F_a$  – along the coordinates of the solvent polarization, the transmission coefficient – along the proton coordinate.

# Electronically adiabatic transitions

Partially adiabatic transitions:

$$\tau_{e(p)} \ll \tau_{p(e)}; \tau_{p(s)} \gg \tau_s$$

# Partially adiabatic transitions



$$\Delta E \approx \frac{1}{2} \hbar \Omega_p \exp(-\sigma_{ad}) \ll k_B T$$

$$\frac{\omega}{2\pi} \kappa_{n.ad.}^{partially} = (\Delta E / 2)^2 \sqrt{\frac{\pi}{\hbar^2 E_r k_B T}}$$

$q_r$  is the reaction coordinate

M.A.Vorotyntsev, R.R.Dogonadze  
A.M.Kuznetsov, 1973

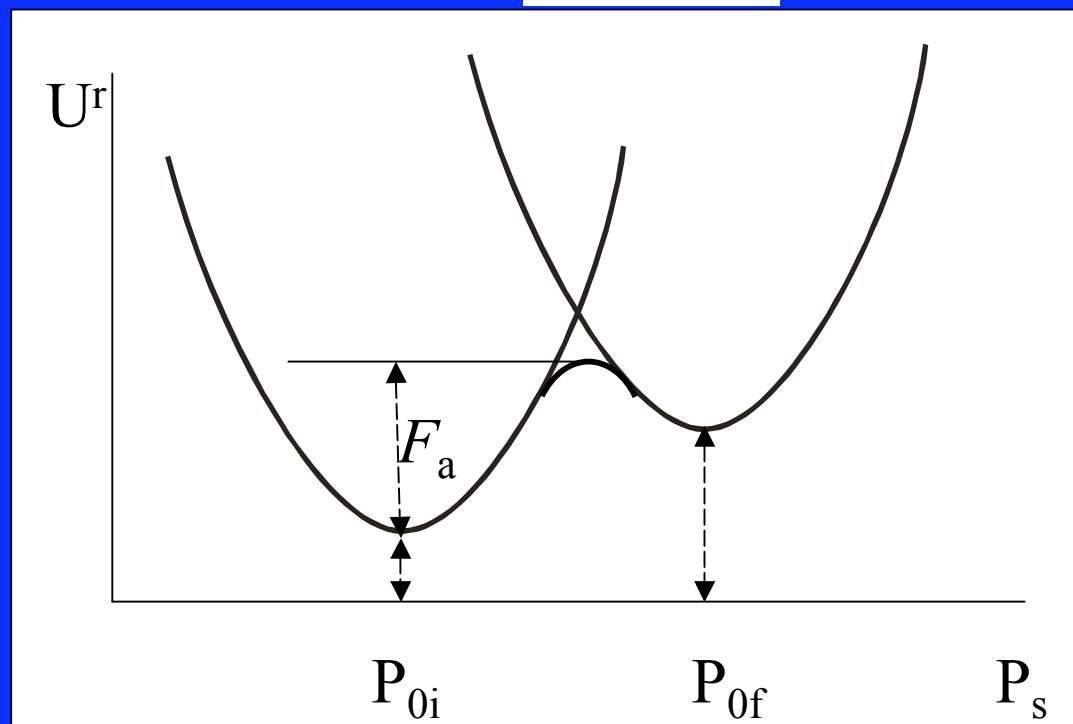
# Totally adiabatic reactions

Electron can follow the motion of the proton, and the proton in its turn also adjusts its state to the motion along the medium coordinates.

$$\Delta E > k_B T$$



$$K_{ad.} = 1$$



Totally adiabatic transitions:

$$\tau_{e(p)} \ll \tau_{p(e)}; \tau_{p(s)} \ll \tau_s$$

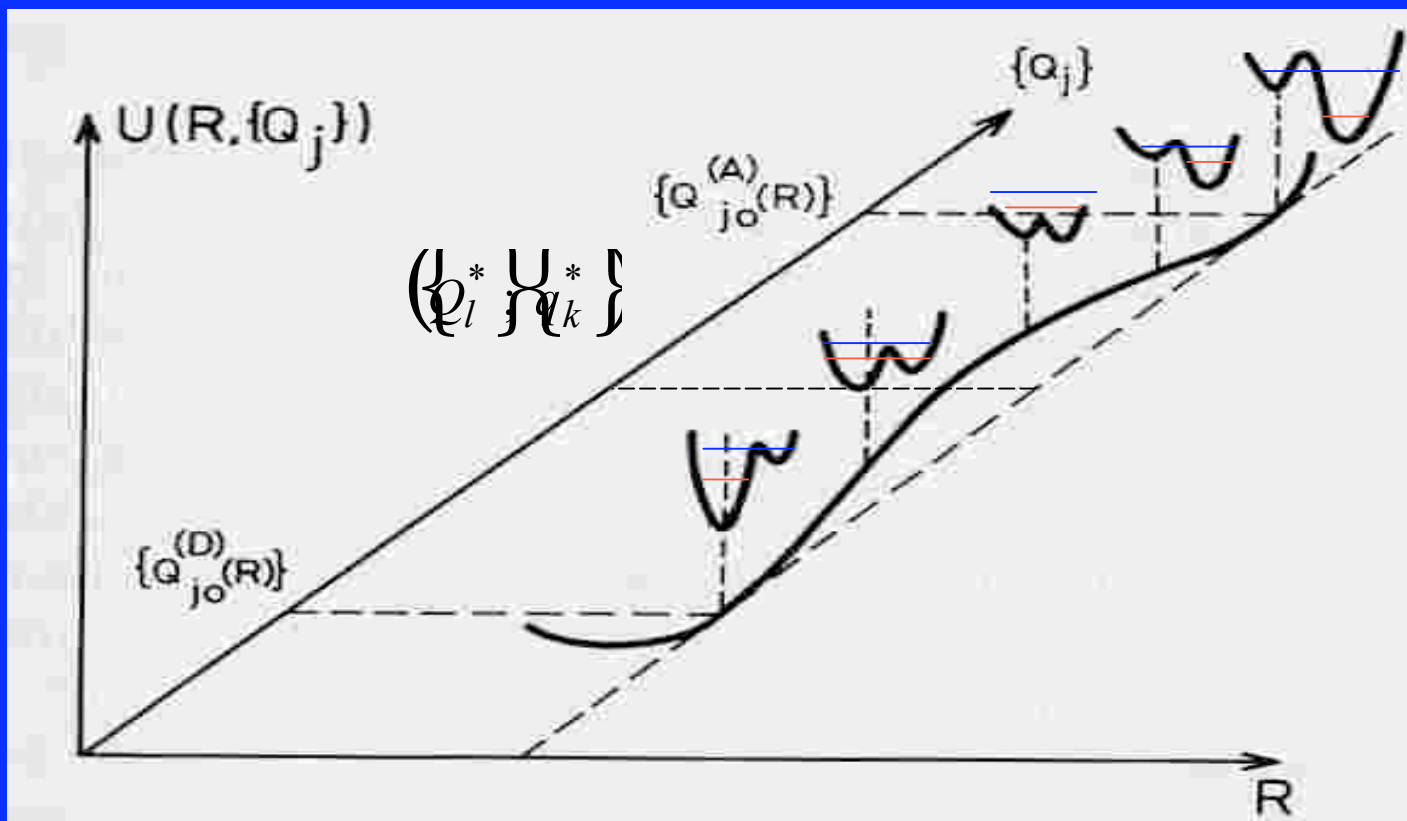
$$F_a^{ad.} \approx F_a^{n.ad.} - \sqrt{\alpha(1-\alpha)}\Delta E$$

$$\Delta E = E_1 - E_0$$

$$U_\alpha(\mathbf{P}) = U_i(\mathbf{P}) + \frac{1}{2} \left[ U_f(\mathbf{P}) - U_i(\mathbf{P}) - \sqrt{[U_f(\mathbf{P}) - U_i(\mathbf{P})]^2 + (\Delta E)^2} \right]$$

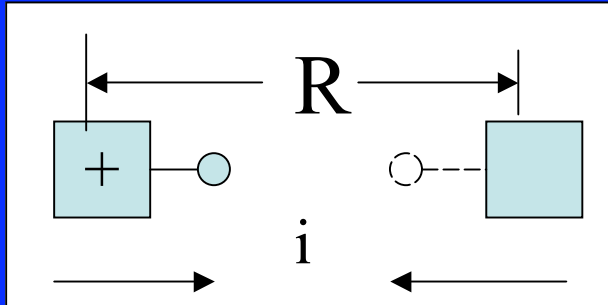


# Physical mechanism



Proton remains in its ground vibrational state

# Promoting modes



$$W \approx \Delta R_p W^p e^{-U(R_p^*)/k_B T}$$

$$U(R) = \frac{1}{2} K (R - R_0)^2$$

$$R_p^* = R_0 / \left( 1 + 2k_B T \alpha_p / K \right)$$

$$\frac{k_H}{k_D} = \frac{\Delta R_H}{\Delta R_D} \frac{W_{00}^H}{W_{00}^D} e^{[U(R_D^*) - U(R_H^*)]/k_B T} =$$

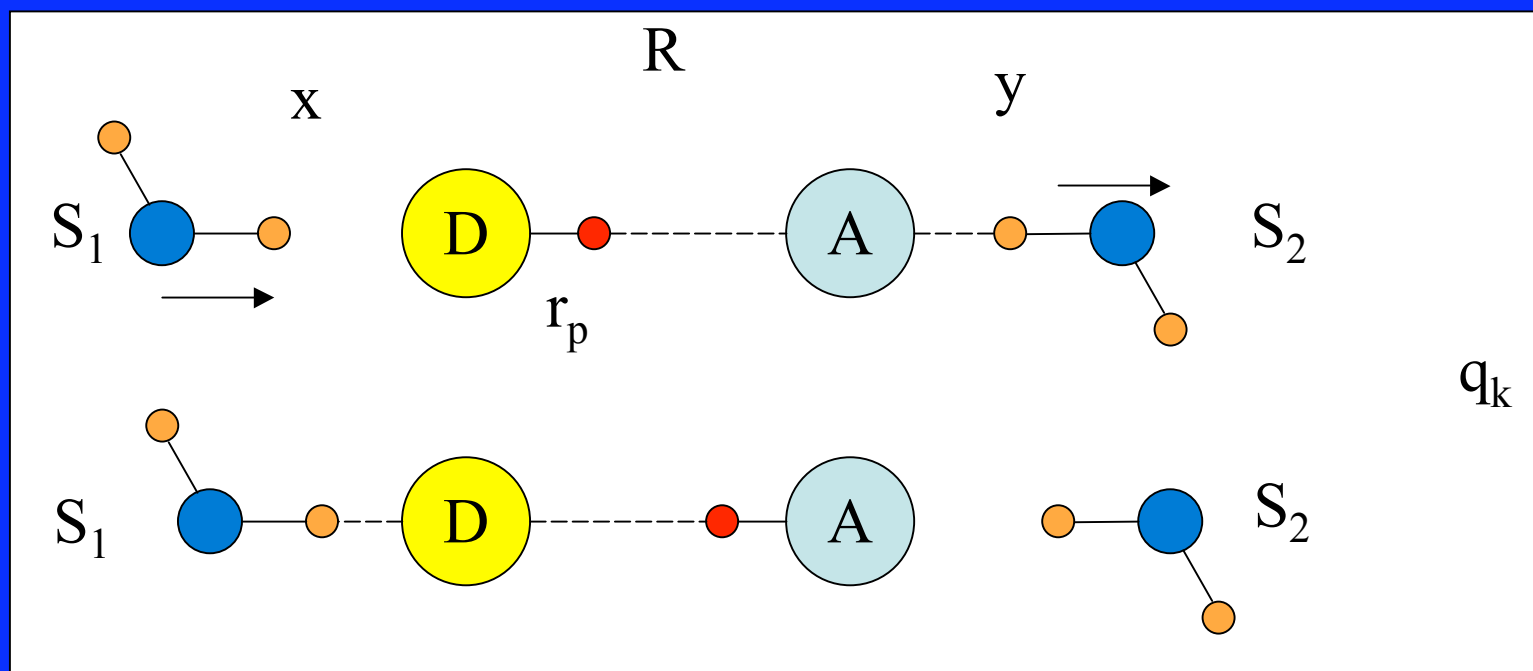
$$\frac{\Delta R_H}{\Delta R_D} e^{\sigma_{00}^D - \sigma_{00}^H} e^{[U(R_D^*) - U(R_H^*)]/k_B T}$$

$$R_H^* > R_D^* ;$$

$$U(R_H^*) < U(R_D^*)$$

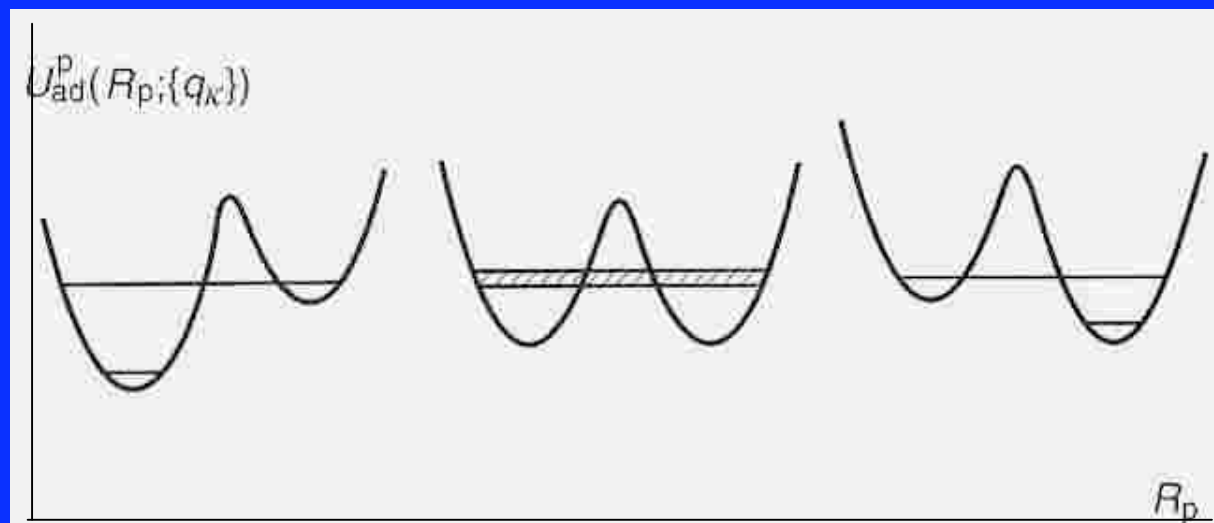
# Proton transfer in hydrogen bonded complexes

$\text{SN}_2$  - mechanism



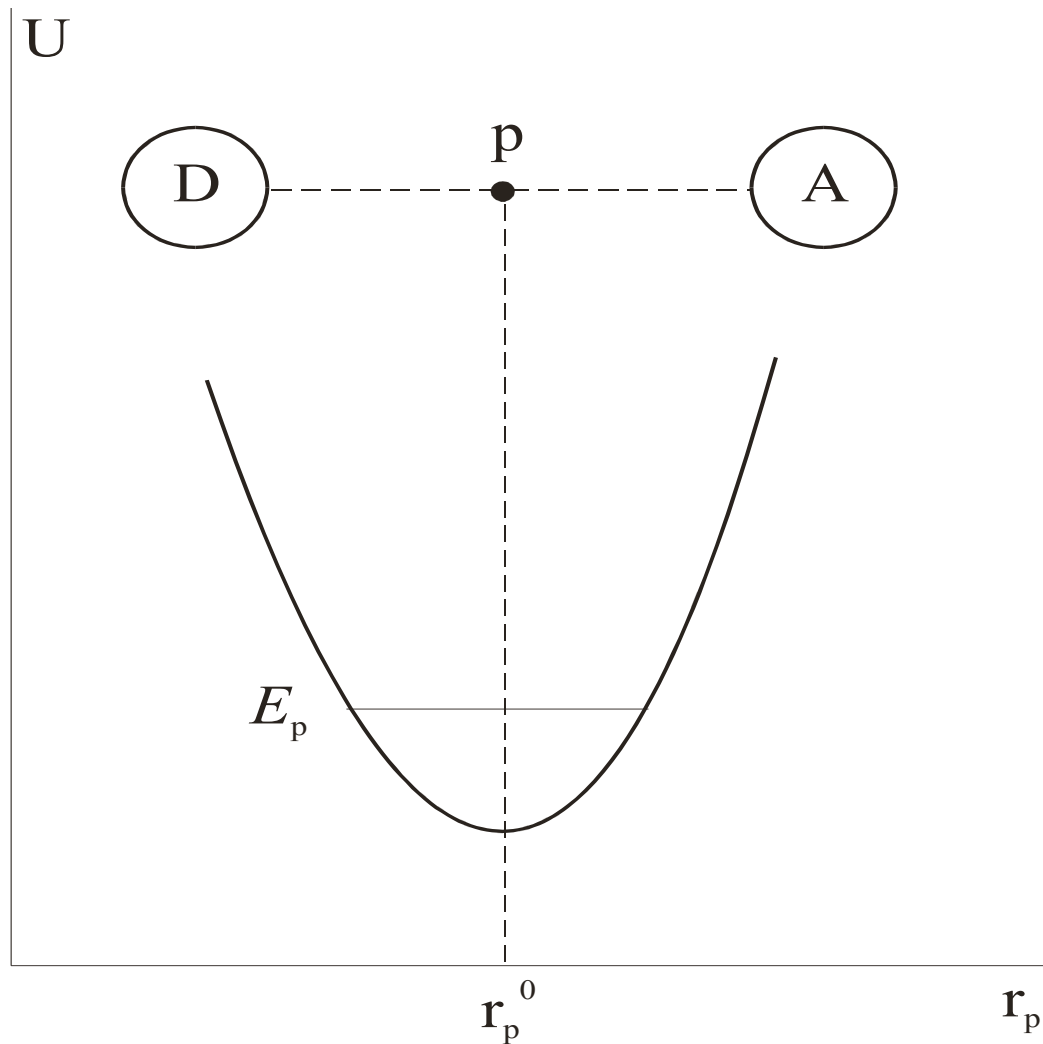
“Synchronous” shift of the molecules  $S_1$  and  $S_2$

# Long hydrogen bonds with a double-well potential for the proton



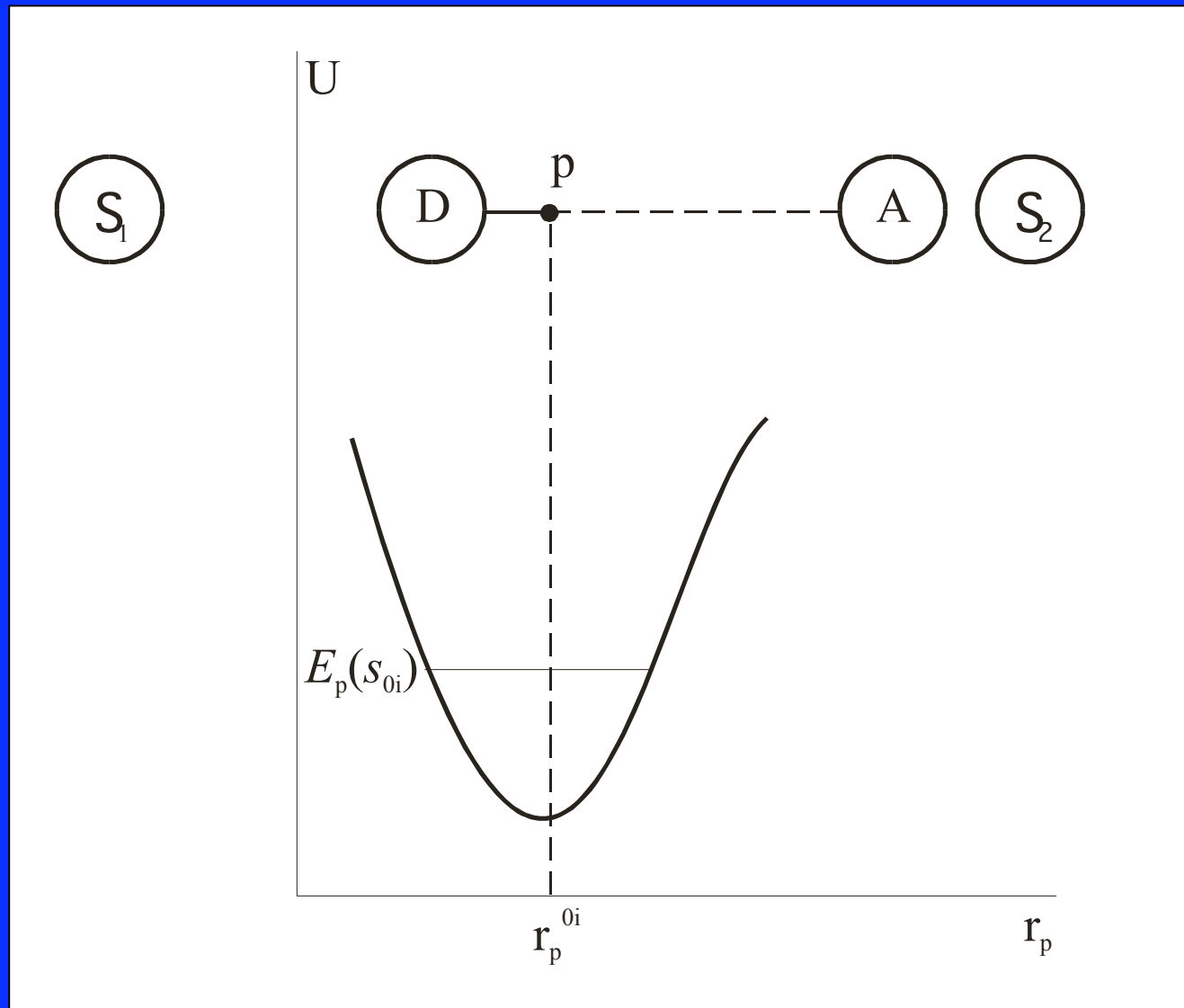
1. Main role belongs here to short-range interactions with nearest molecular environment.
2. The solvent reorganization energy is small or zero here.

# Short hydrogen bonds with a single-well potential for the proton

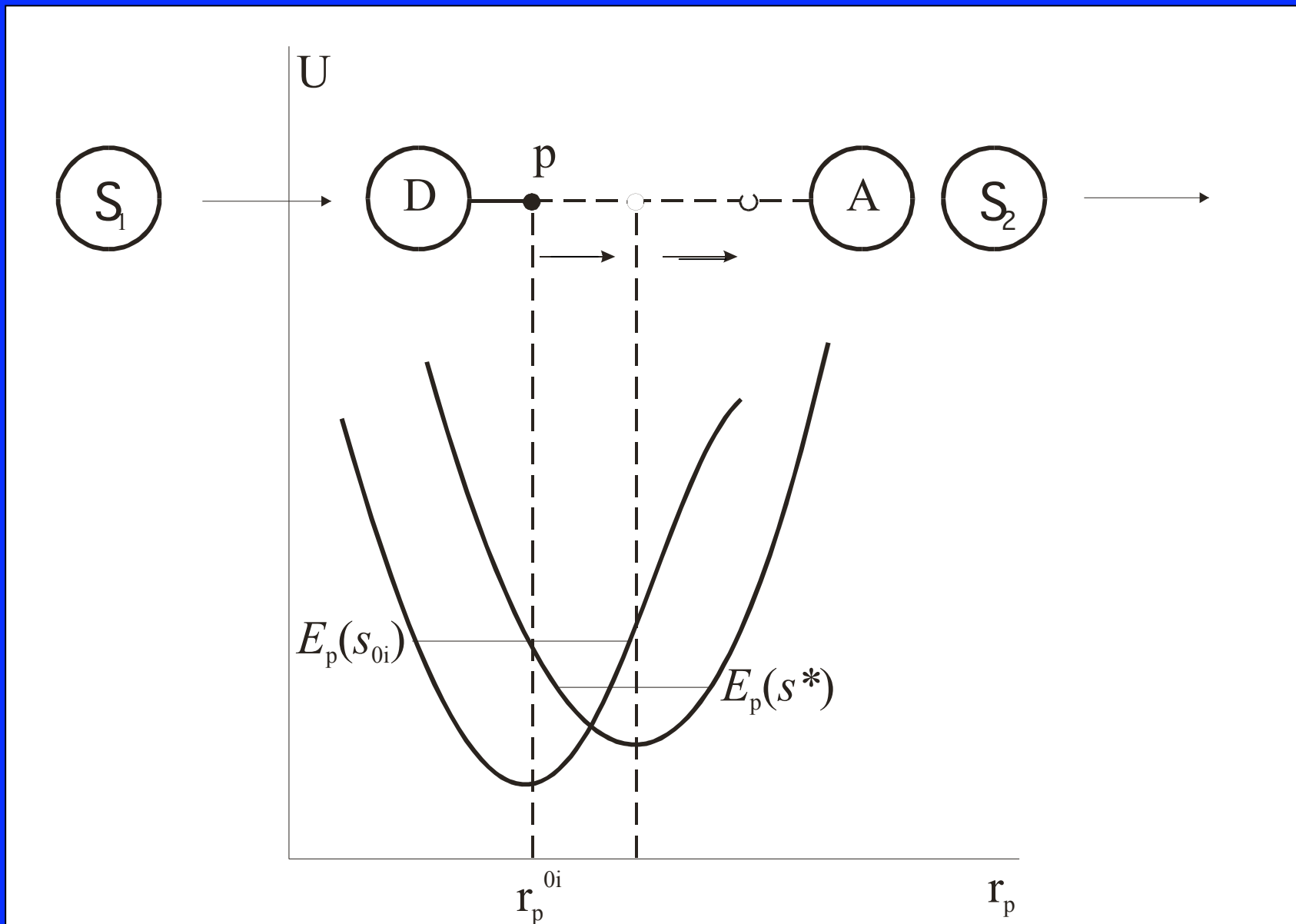


A.M.Kuznetsov, J.Ulstrup,  
2005

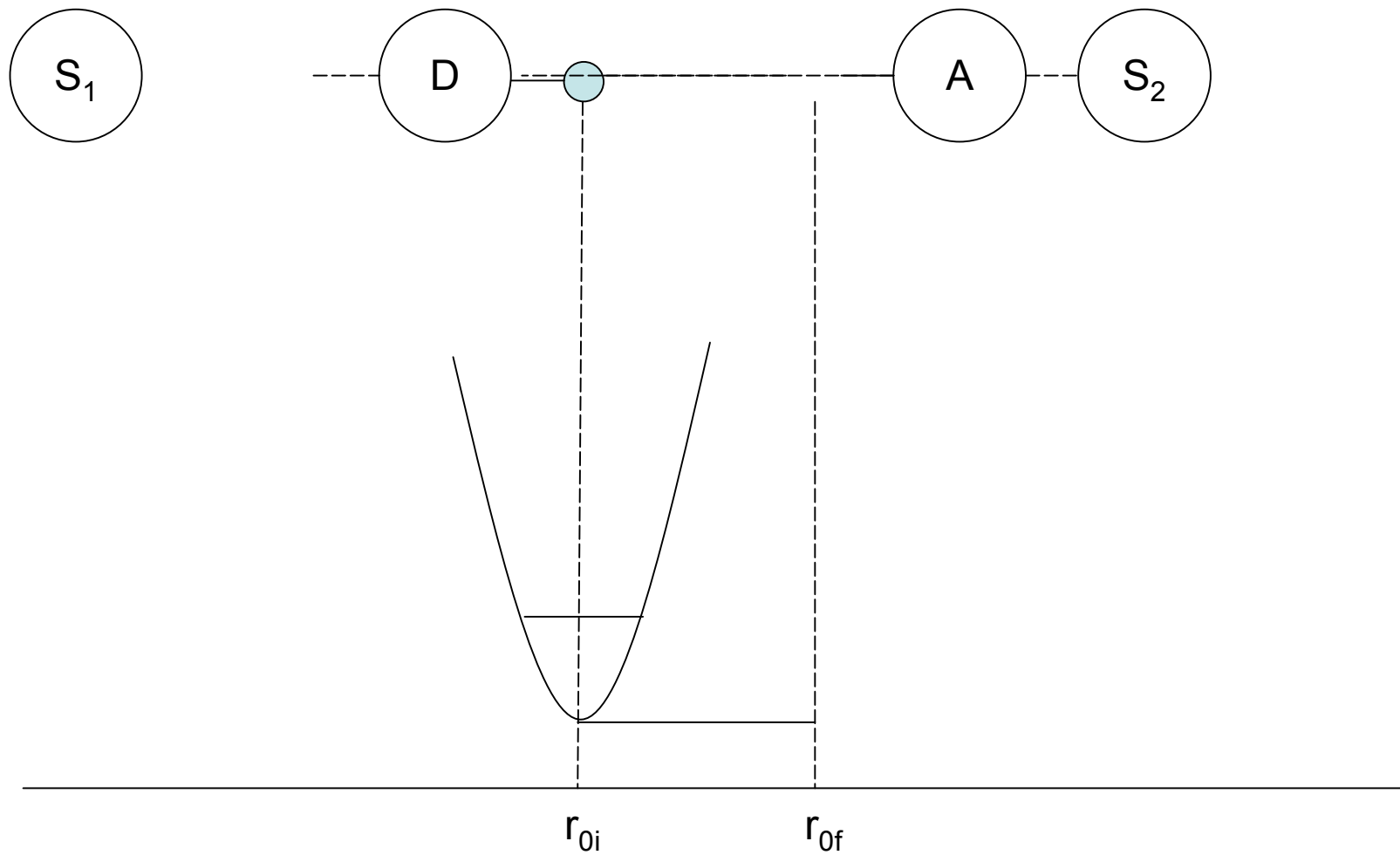
Initial state of the complex with short hydrogen bond with a single-well potential for the proton



# Initial and transition states of the short-hydrogen bond-complex with a single-well potential for the proton



# A scheme of the transition (SN2-mechanism)





# Activation free energy and kinetic isotope effect

## Adiabatic free energy surface

$$U(s) = V_{sc}(s) + E_p(s)$$

M.A.Vorotyntsev, R.R.Dogonadze  
A.M.Kuznetsov, 1973  
A.M.Kuznetsov, 1997  
P.M.Kiefer, J.T.Hynes, 2003

## Activation free energy

$$G^\ddagger = V_{sc}(s^*) - V_{sc}(s_{0i}) + [E_p(s^*) - E_p(s_{0i})]$$

## Kinetic isotope effect

$$\frac{k_H}{k_D} \approx \frac{\omega_H}{\omega_D} \exp \left\{ \frac{[E_D(s^*) - E_D(s_{0i})] - [E_H(s^*) - E_H(s_{0i})]}{k_B T} \right\}$$

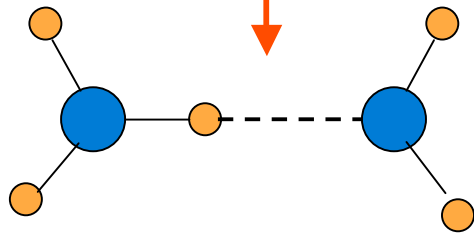
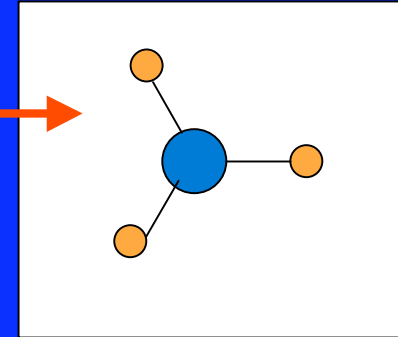
# Proton transfer in water

Three main structural  
units:

Free hydroxonium ions

Eigen clusters

Zundel clusters

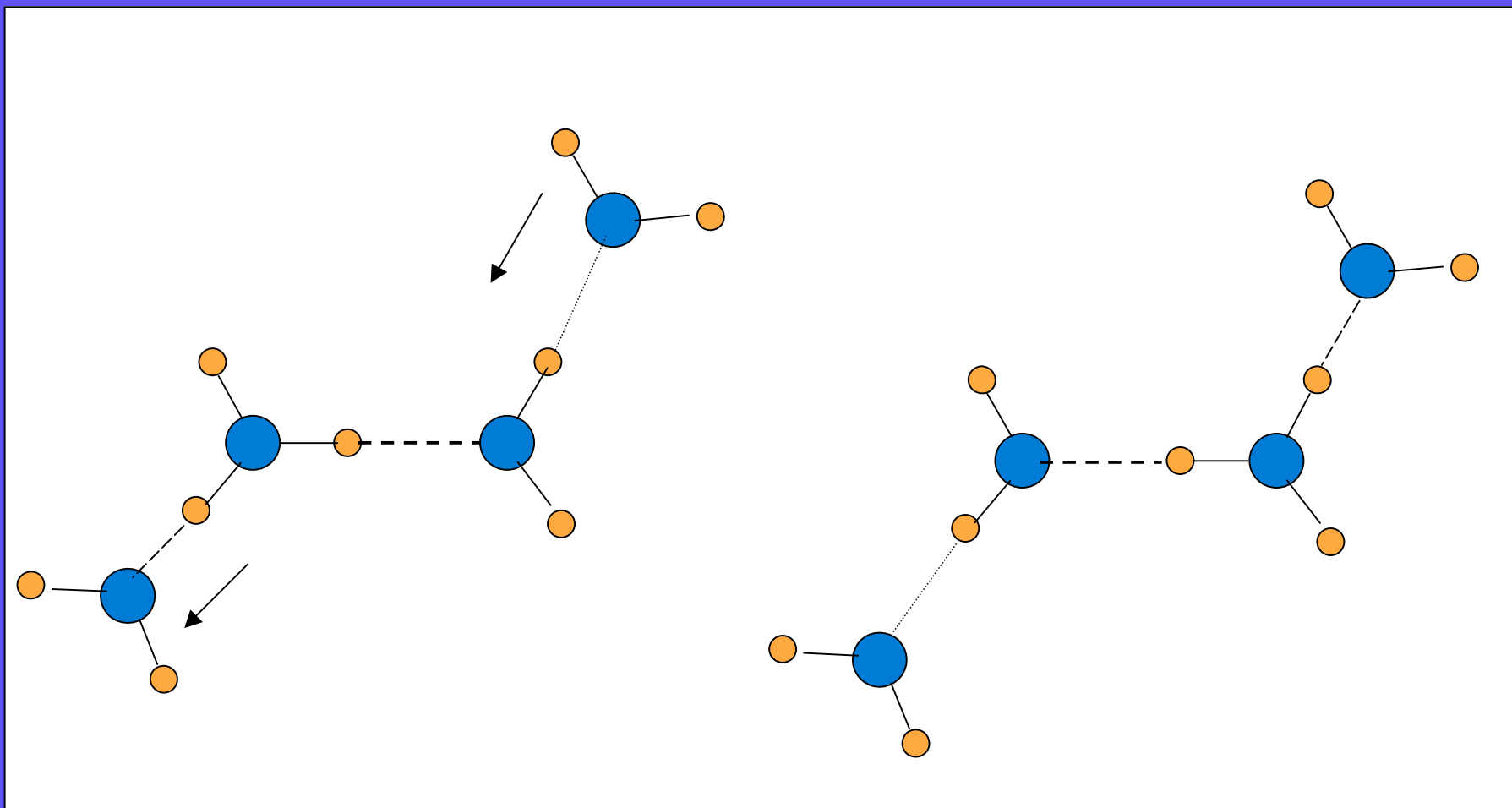


Two major transfer mechanisms:

Classical diffusion of the hydroxonium ions

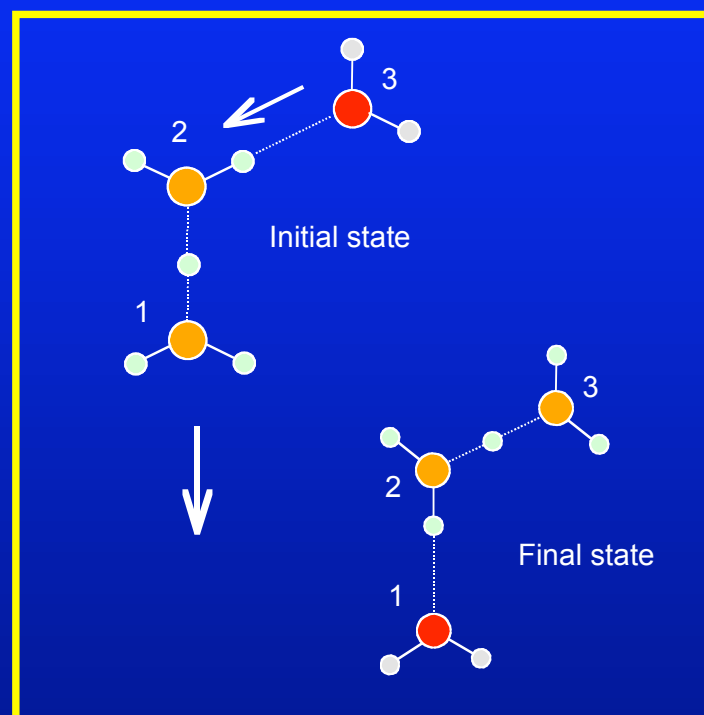
Structural diffusion of clusters

# A scheme of proton transfer between two water molecules

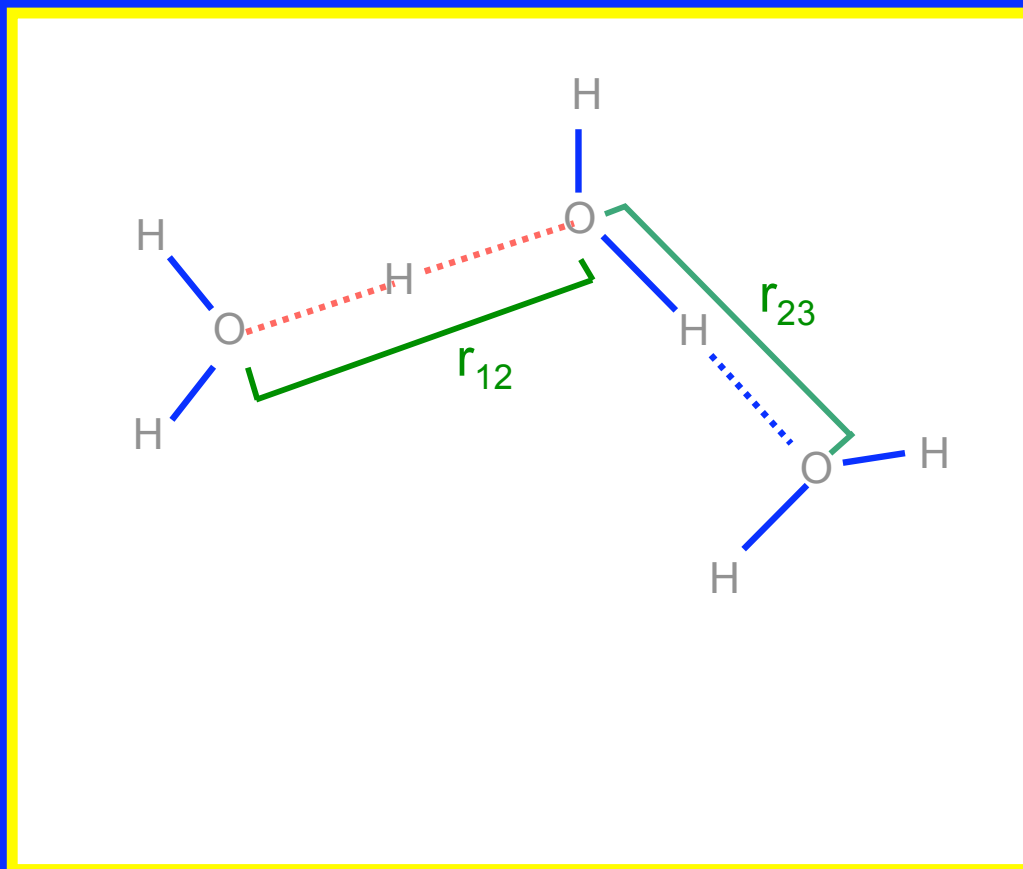


# A scheme of proton transfer with the formation of the nearby Zundel complex

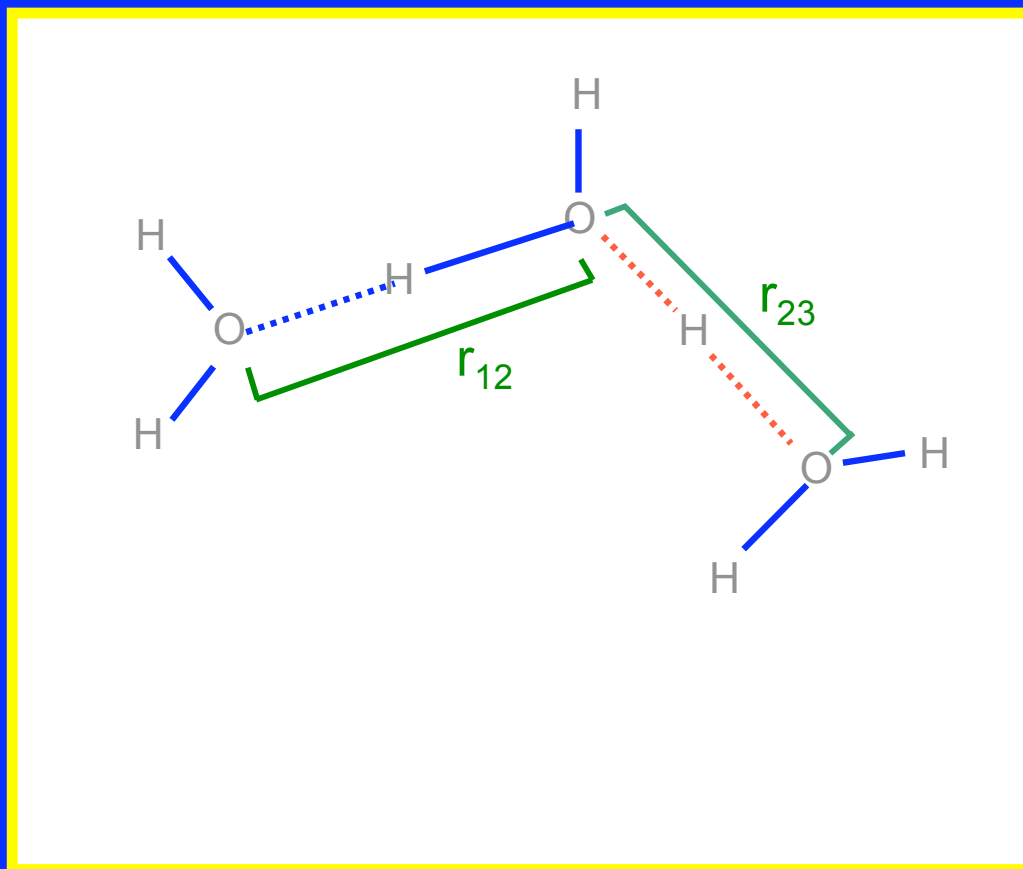
A scheme of proton transfer via the transition of two protons in a molecular triad



Distances between oxygen atoms  $r_{12}$ ,  $r_{23}$   
Initial complex

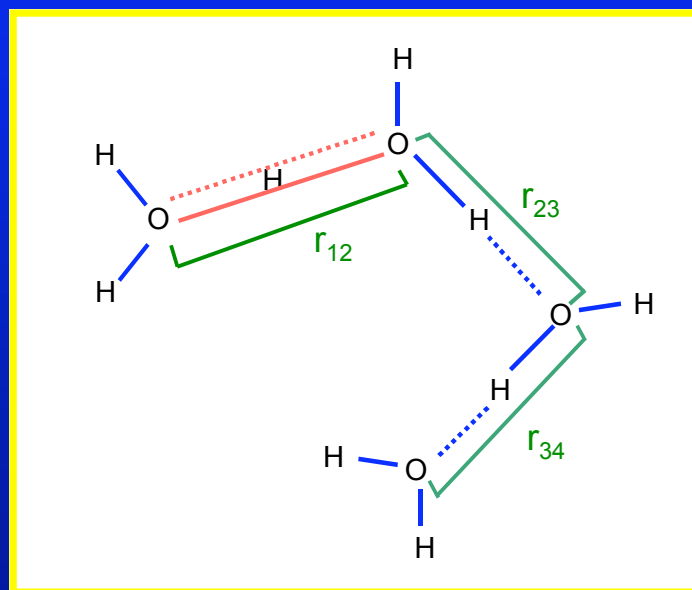


Distances between oxygen atoms  $r_{12}$ ,  $r_{23}$   
Adjacent complex



# Coordinates for the transitions between remote Zundel complexes

Definitions of the distances  $r_{12}$ ,  $r_{23}$  and  $r_{34}$

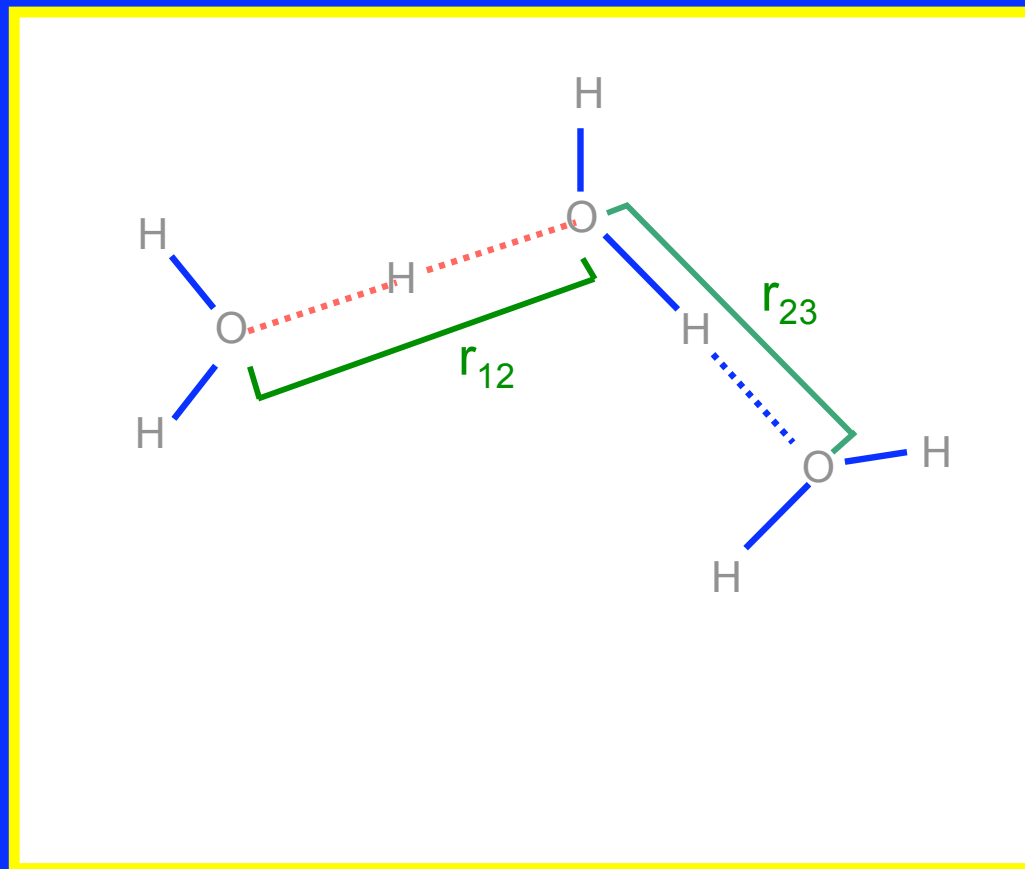


## Relationship with MDS

1. The estimation of the time when the distance between the proton and some oxygen atom becomes located within a certain interval of values is insufficient for the conclusions on the mechanism of the mobility and its value.
2. A more consistent way is the calculation of the probability of formation of statistically equivalent structures of heavy atoms (with an excess proton in a certain region) since the translocation of the proton in such systems is entirely determined by structural fluctuations of heavy atoms of the nearest molecular environment.
3. The approach of an excess proton to one of the oxygen atoms in the situation where other atoms do not form appropriate configuration does not result in irreversible proton transfer and overestimates the mobility. This event is followed by fast reversed transition of the proton. (S.Walbran & A.A.Kornyshev, 2001, A.A.Kornyshev, A.M.Kuznetsov, E.Spohr, J.Ulstrup, 2003)

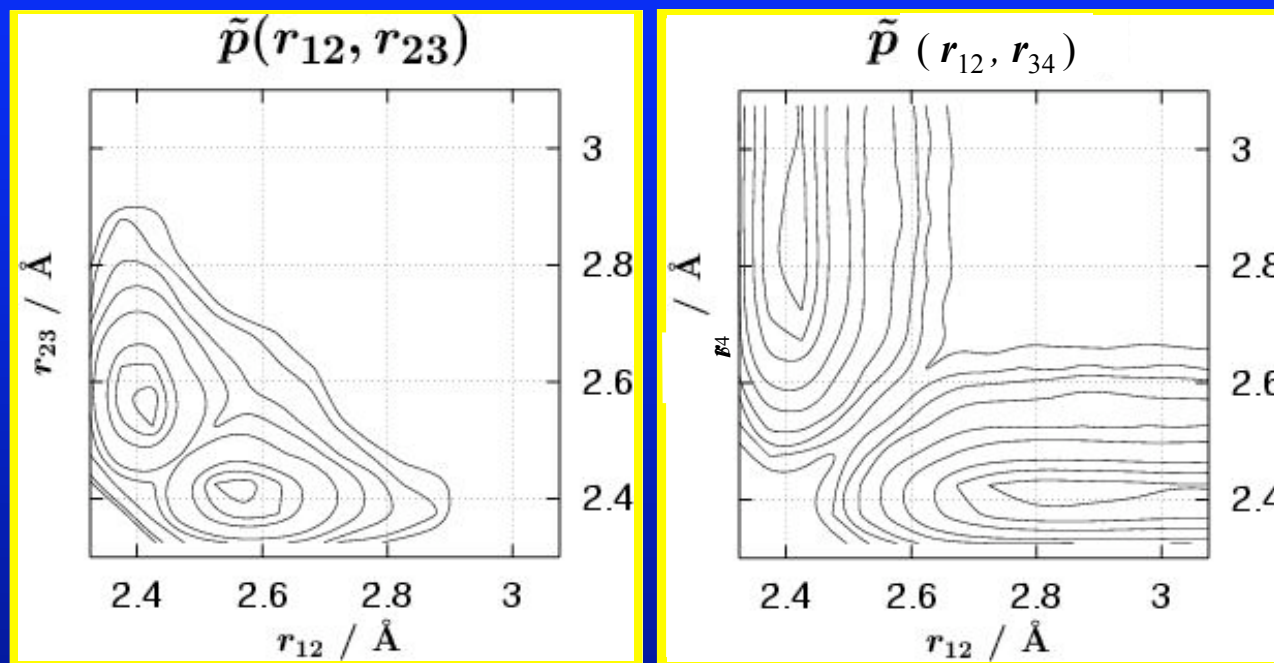


Zundel-to-Zundel transitions (the O-O distances  $r_{12}$ ,  $r_{23}$  and  $r_{34}$  )



# Probability distributions

## Probability distribution



A.A.Kornyshev, A.M.Kuznetsov, E.Spohr, J.Ulstrup,  
J.Phys.Chem.B, 107 (2003) 3351-3366

## Concluding remarks

1. Existing theoretical models shed light on the microscopic mechanisms of elementary proton transitions which may take place in various physical situations and in combination with realistic potentials (e.g. extracted from *ab initio* calculations) may serve as a basis for quantitative estimations of proton mobility. Computer simulations may allow to discriminate between different limiting situations which are the subject of the models.
2. Proton transfer in hydrogen bonded systems proceeds by “SN2-mechanism” and is determined mainly by structural fluctuations in the vicinity of the proton transfer complex. The reorganization of macroscopic polarization of the medium plays minor role in these systems.

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