



# Lecture #5 of 12

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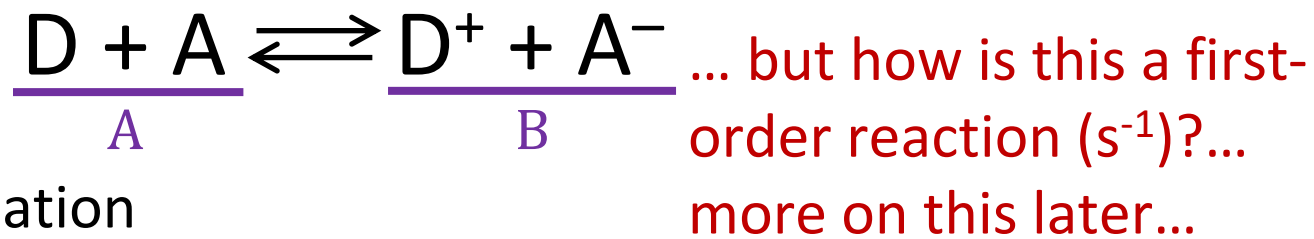
# Thermal (Dark) Reactions

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# Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}k_{\text{B}}T}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{k_{\text{B}}T}\right) \dots \frac{2\pi |H_{\text{DA}}|^2}{\hbar \sqrt{4\pi\lambda k_{\text{B}}T}} \text{ has units of s}^{-1}$$



Eyring–Polanyi–Evans (1930s)

theoretical rate constant equation (from **transition-state theory / activated complex theory**)

$$k_f = \kappa \nu K^{\ddagger} = \frac{\kappa k_{\text{B}}T}{h} K^{\ddagger} \quad \dots \text{with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu \text{ (s}^{-1}\text{)}$$

... and  $R = N_A k_{\text{B}} \dots$  and  $\frac{\kappa k_{\text{B}}T}{h}$  has units of  $\text{s}^{-1}$

$$k_f = \frac{\kappa k_{\text{B}}T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) = \frac{\kappa k_{\text{B}}T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \quad \dots \text{and so } A \text{ contains } \Delta S^{\ddagger}$$

... what is the largest predicted pre-exponential factor at 25 °C?  **$(161 \text{ fs})^{-1} = (1.61 \times 10^{-13} \text{ s})^{-1}$**

# Outer + Inner Reorganization Energies

## Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

**This theory came about by answering the following question:** For an electron-transfer event, how does one satisfy the Franck–Condon principle and the conservation of energy?

- Franck–Condon principle: Nuclei are fixed during electron-transfer between orbitals... Born–Oppenheimer approximation is relevant

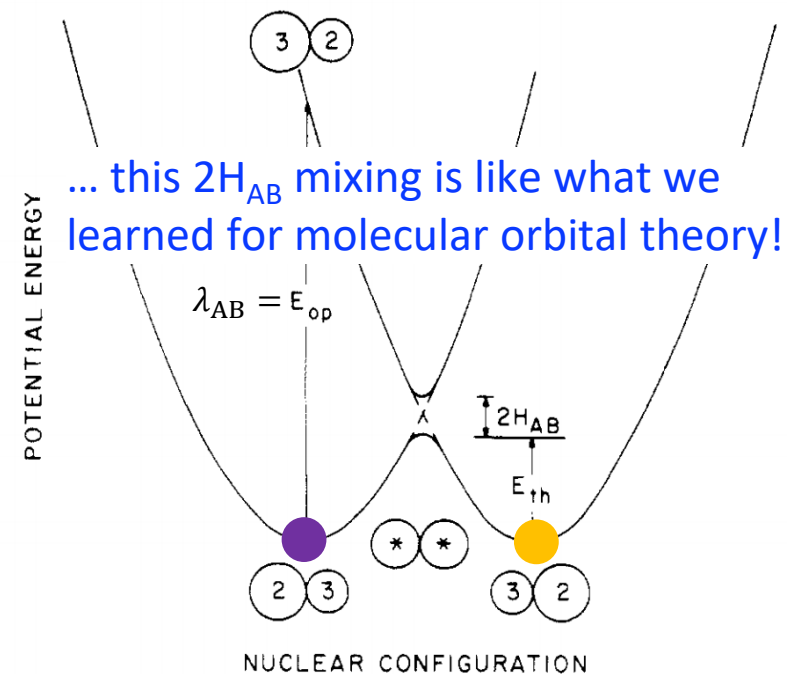
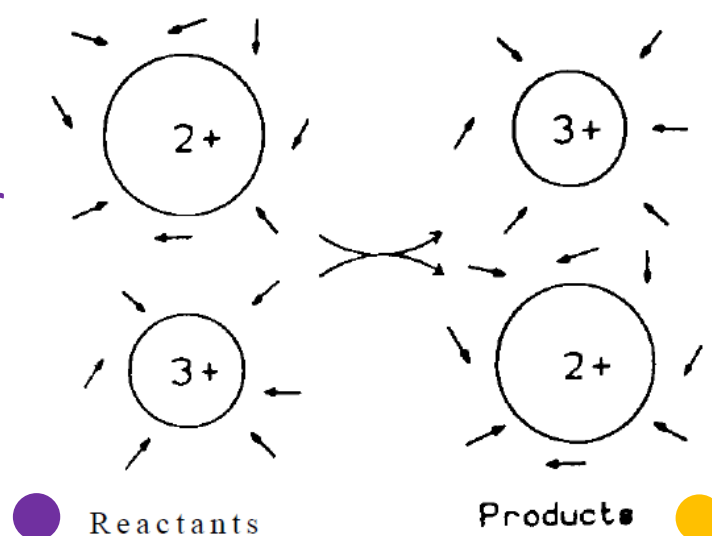
$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2} \sum_l f_l (\Delta q_{e,l})^2$$

... this is for a harmonic oscillator  
... with force constants,  $f_l$ ...

... and yes, it's another parabola!

## Electron Transfer in Solution

$$\lambda_{AB} = \lambda_{in} + \lambda_{out}$$



# Observation of Inverted Region Behavior

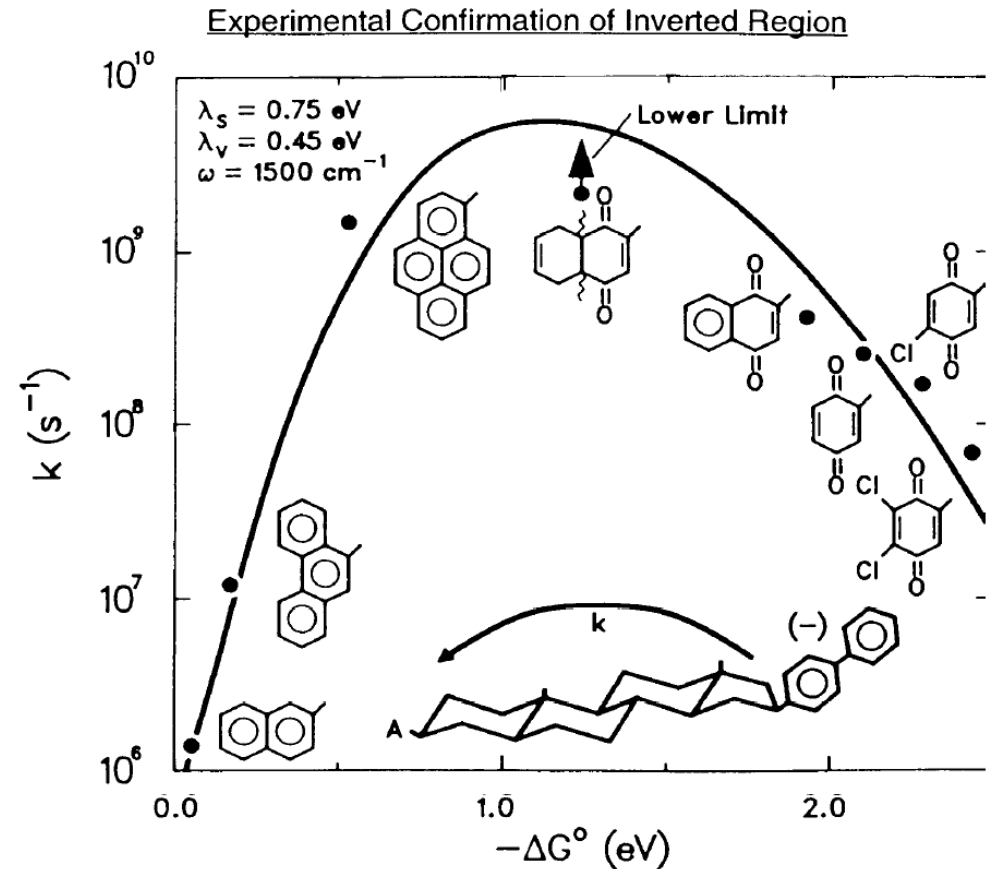
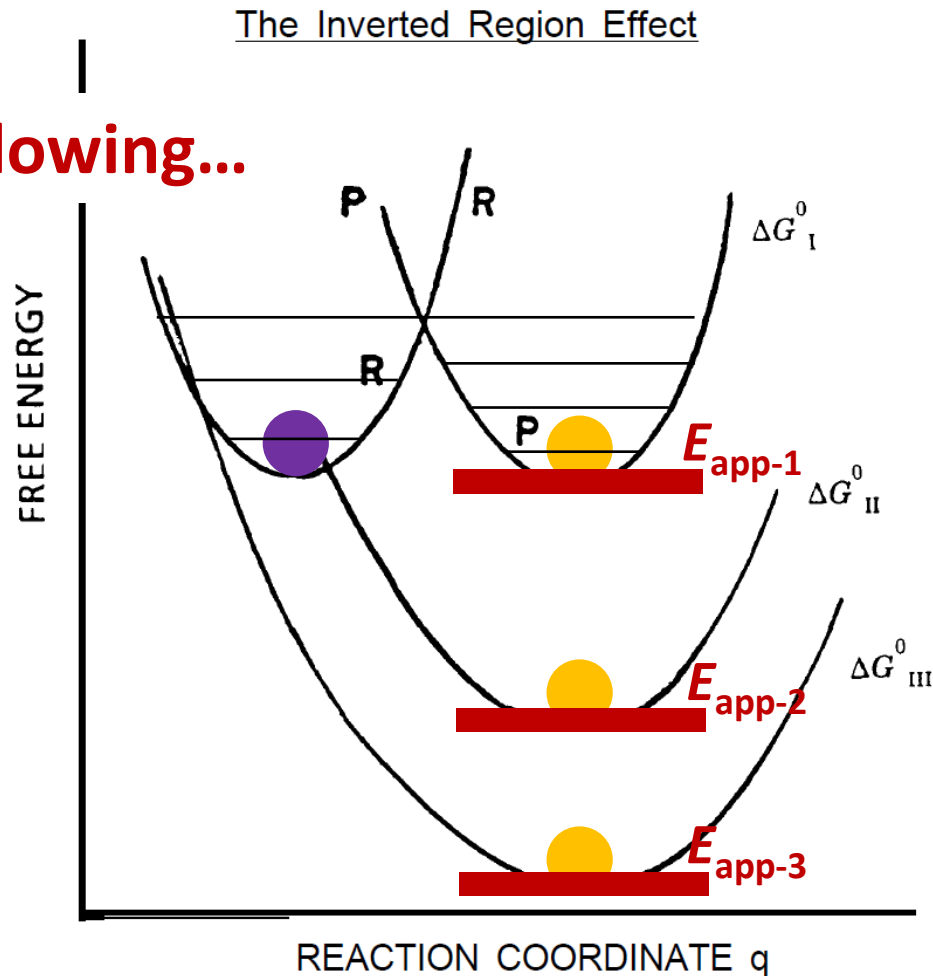
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

Cross–Miller (1984)

observation of inverted region

**Foreshadowing...**



L. T. Calcaterra, J. R. Miller & G. L. Closs, *J. Am. Chem. Soc.*, **1984**, *106*, 3047–3049

G. L. Closs & J. R. Miller, *Science*, **1988**, *240*, 440–447

# Today's Critical Guiding Question

*What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species... and uniquely for today, how does it allow us to quantitatively predict kinetic information... for real this time: Part 2?*

# Thermal (Dark) Reactions

- Activation energy, Eyring–Polanyi–Evans equation
- Marcus–Hush (electron-transfer) theory
- Transition-state character, Reorganization energies (outer and inner), **Linear free energy relationships**
- **Molecular orbital theory, Huang–Rhys factor**
- **Quantum mechanical tunneling, Superexchange**
- **Inner *versus* Outer sphere reactions, Robin–Day classification**
- **Self-exchange reactions, Marcus cross relations**
- **Charge transfer across electrified interfaces, Butler–Volmer equation, Rate-determining step, Fermi’s golden rule, Marcus–Gerischer theory**

# Linear Free Energy Relationships (LFERs)

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

Brønsted–Pedersen (1924)

empirical LFER for proton transfer

$$\ln k_{\text{PT}} = -\beta \text{p}K_{\text{a}} + C$$

$$\ln k_{\text{PT}} = \beta \Delta \text{p}K_{\text{a}} + C'$$

Brønsted slope...

... most people use  $\alpha$ ...

... but I prefer  $\beta$

... like in EChem

**linear free-energy relation** Online use... < >

Also contains definition of: [linear Gibbs energy relation](#)

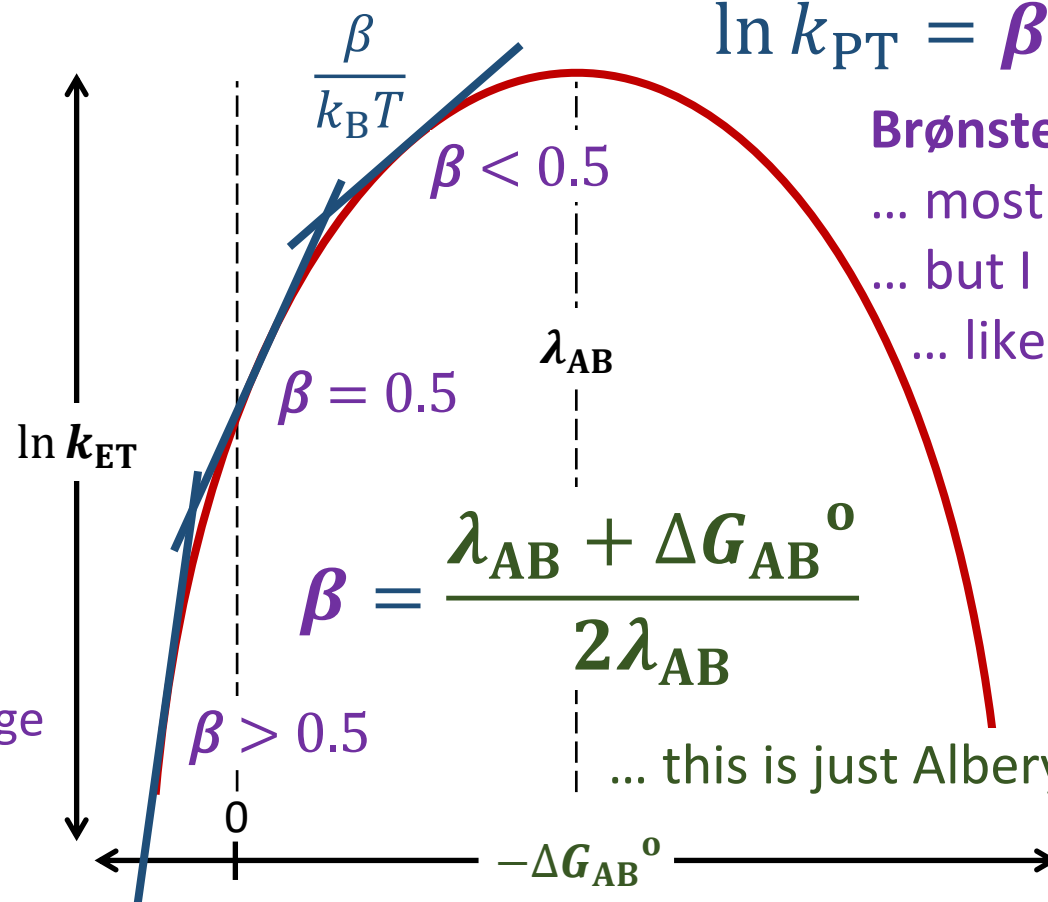
A linear correlation between the logarithm of a [rate constant](#) or [equilibrium constant](#) for one series of reactions and the logarithm of the [rate constant](#) or [equilibrium constant](#) for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy relations) are the [Brønsted relation](#), and the [Hammett equation](#).

The name arises because the logarithm of an [equilibrium constant](#) (at constant temperature and pressure) is proportional to a standard [free energy](#) (Gibbs energy) change, and the logarithm of a [rate constant](#) is a linear function of the [free energy](#) (Gibbs energy) of [activation](#).

It has been suggested that this name should be replaced by linear Gibbs energy relation, but at present there is little sign of acceptance of this change. The area of physical organic

Cite as: IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. <https://doi.org/10.1351/goldbook>.

Last revised: February 24, 2014



... trend looks linear over a small enough  $\Delta G_{\text{AB}}^{\circ}$  range

J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, 31, 227–263

R. A. Marcus, *Farad. Discuss. Chem. Soc.*, **1982**, 74, 7–15



# Marcus Kinetic Behavior

**Table 13** Applications of the Marcus relation

<b>Electron transfers</b>	<b>Electrochemical</b>	<b>Tafel Law</b> <b>Electrode kinetics at semiconductors</b>
	<b>Homogeneous</b>	<b>Correlation with electrochemical</b> <b>Cross reactions obey Marcus relation (Eq. 4)</b>
<b>Proton transfers</b>	<b>Marcus relation reduces to Brønsted Law</b>	<b>Explains curved Brønsted plots</b>
	<b>O, N bases and some transfers to C</b> <b>Concerted reactions</b>	<b>Describes enolization of acetone</b>
<b>Methyl transfers</b>	<b>Cross reactions obey Marcus relation</b> <b>Swain-Scott <math>n</math> separated into <math>n^{\ddagger}</math> and <math>n^{\theta}</math></b> <b><math>\alpha D</math> isotope effects measure <math>C^+</math> character</b>	
<b>Nucleophilic additions</b>	<b>Provides alternative explanation to Ritchie relation</b> <b>Values of <math>\bar{G}</math> found to be constant for similar species</b>	

# Schrödinger Equation

But you still didn't tell us why we need to recall this equation

$$\hat{H}\psi_n(x) = (\hat{T} + \hat{V})\psi_n(x) = E_n\psi(x)$$

... we need to fill **internal energies**,  $E_n$ , with particles... okay.

Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\epsilon} \quad \mathbf{E} = -\frac{\partial \phi(x)}{\partial x}$$

$$\phi(r) = \frac{q}{4\pi\epsilon r}$$

for a point charge...  
look familiar?

... and that under most chemical conditions, potential energy,  $\hat{V}(x)$ , is **electrostatic**,  $\phi(x)$

... which is actually not so limiting because there are only 4-ish forces of Nature

... and while we're at it, let's (re)learn **overlap integral** ( $S_{nm}$ ), **expectation value** ( $\langle p_n \rangle$ ), **bra-ket notation** ( $\langle \psi_n | \psi_m \rangle$ ), and exponential **tunneling probability**...

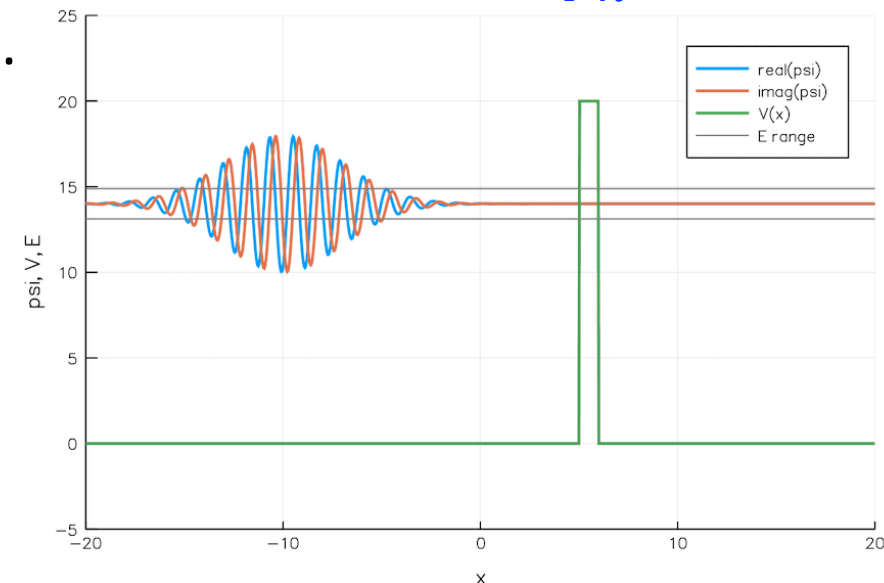
$$\text{Probability Density}(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$$

... with  $\psi_n^*(x)$  (complex conjugate)

$$\text{Overlap integral, } S_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x) dx = \langle \psi_n | \psi_m \rangle$$

... with  $\langle \Psi_n |$  ("bra") and  $|\Psi_m \rangle$  ("ket")

$$\text{Mean Energy, } \langle E_n \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\hat{H}\Psi_n(x,t)dx}{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_n(x,t)dx} = \langle \Psi_n | \hat{H} | \Psi_n \rangle = \langle \hat{H} \rangle$$



# Molecular Orbital Theory

## Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{kT}\right)$$

quantum adiabatic  
electronic coupling

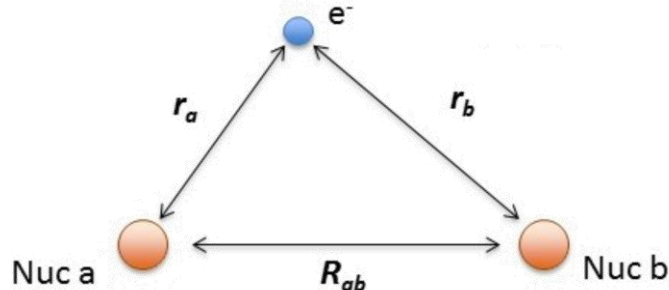
classical nuclear free-  
energy dependence

... remember the simplicity of  $\text{H}_2^+$ ... which resembles  $\lambda_{\text{out}}$  math

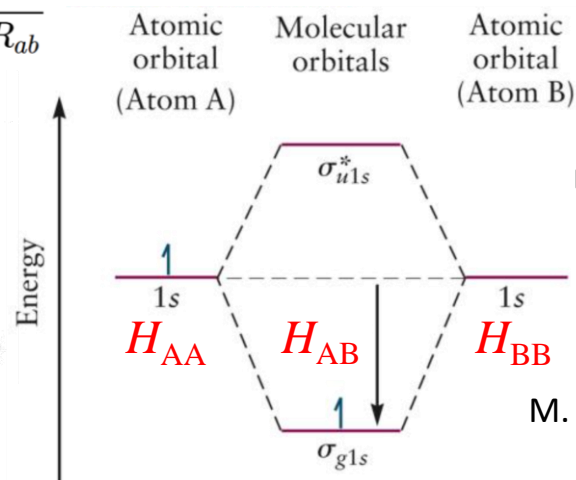
$$\hat{H}(r, R_{ab}) = -\frac{\hbar^2}{2m} \nabla_a^2 - \frac{\hbar^2}{2m} \nabla_b^2 - \frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

matrix

$$\hat{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$



$$E_{\pm}(R) = \frac{1}{1 \pm S(R)} (H_{AA}(R) \pm H_{AB}(R))$$

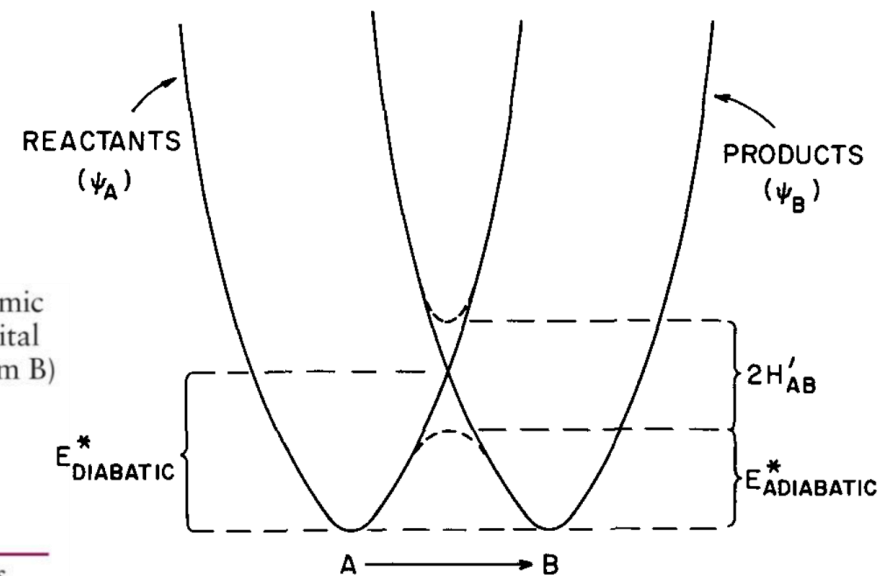


## Molecular Orbital Theory

linear combination of atomic orbitals

(50) The splitting at the intersection is only equal to  $2H_{\text{AB}}$  when the overlap of the electronic wave functions can be neglected. More generally it is equal to  $2(H_{\text{AB}} - S_{\text{AB}}H_{\text{AA}})/(1 - S_{\text{AB}}^2)$  where  $S_{\text{AB}} = \langle \psi_A | \psi_B \rangle$ .

... which equals  $(E_+ - E_-)$  from MO Theory



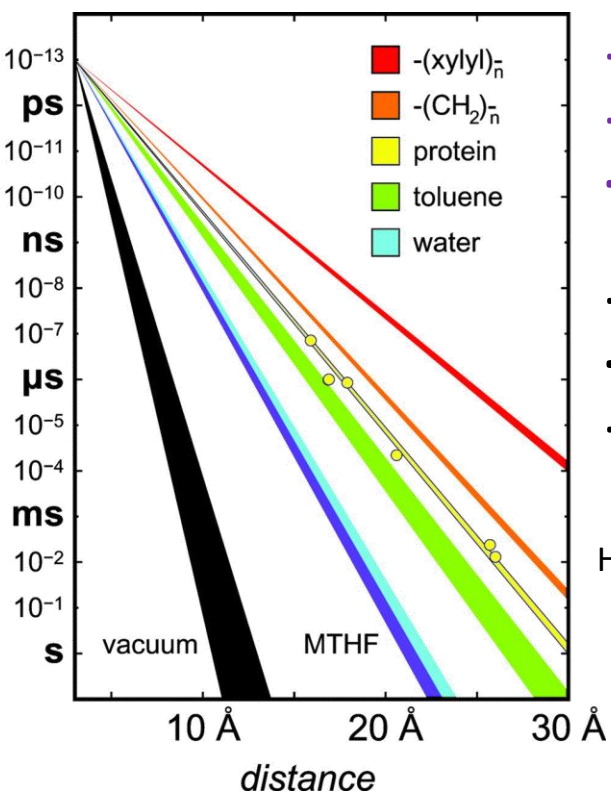
M. D. Newton, *Int. J. Quantum. Chem.*, **1980**, *18*, 363–391  
N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

# Quantum Mechanical Tunneling / Superexchange

## Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{kT}\right)$$



... although through-space tunneling is legit...  
 ... it requires overlap of small wavefunction tails...  
 ... **how does long-distance electron transfer occur?**

... incoherent multi-step hopping...  
 ... **or coherent superexchange...**  
 ... where  $\beta_{\text{eff,hop}} \ll \beta_{\text{super}} < \beta_{\text{tunnel}}$

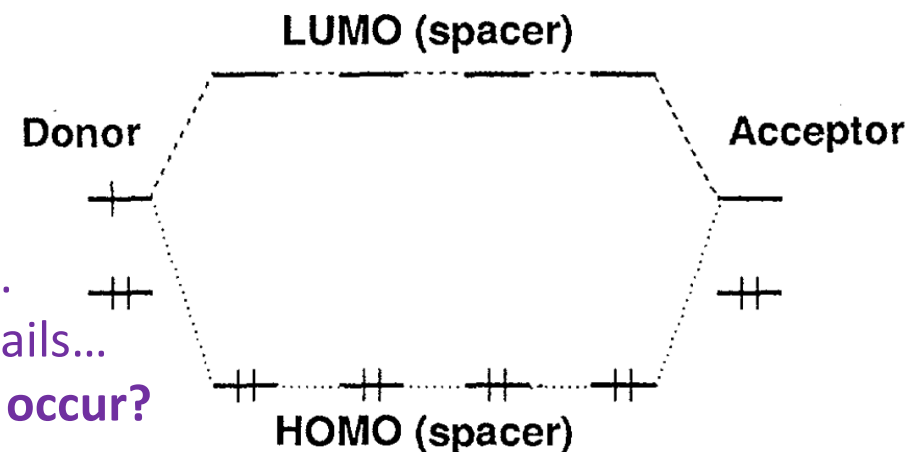
H. B. Gray & J. R. Winkler, *PNAS*, **2005**, *102*, 3534–3539

$$|\hat{H}_{\text{DA}}| = |\langle \Psi_{\text{D}} | \hat{H}_{\text{DA}} | \Psi_{\text{A}} \rangle| = |\hat{H}_{\text{DA}}^{\circ}| \exp\left(-\frac{\beta_{\text{tunnel}}(z_{\text{DA}} - z_{\text{DA}}^{\circ})}{2}\right)$$

... where  $\beta_{\text{tunnel}}$  has units of  $\text{\AA}^{-1}$

## Superexchange (*not hopping!*)

long-distance through-bond transport



$$|\hat{H}_{\text{DA}}| = |\hat{H}_{\text{DA}}^{\circ}| \exp\left(-\frac{\beta_{\text{super}}(N - 1)}{2}\right)$$

... where  $N$  is the number of bonds

G. L. Closs & J. R. Miller, *Science*, **1988**, *240*, 440–447

# Inner versus Outer Sphere Reactions

## Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{kT}\right)$$

## Creutz–Taube ion (1969)

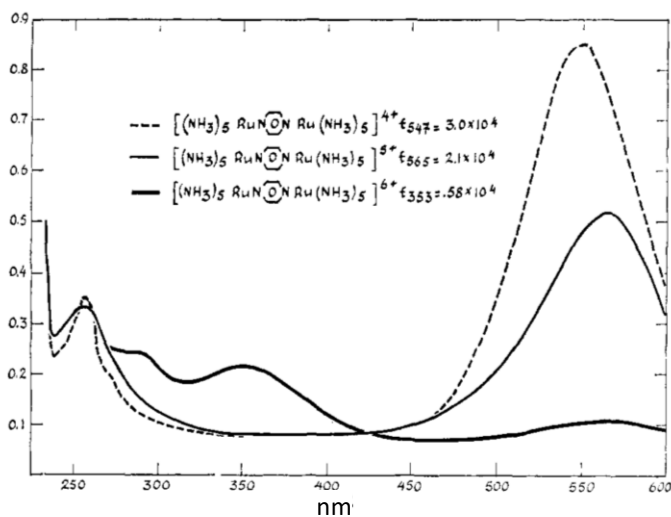


Figure 1. Visible-ultraviolet spectra of [2,2], [2,3], and [3,3] in 0.05  $N$   $\text{HClO}_4$ . (Absorbance around 560 nm for [3,3] is probably due to residual [2,3] in the solution; photoreduction of [3,3] takes place readily.)  $\epsilon_{[2,2]}$  and  $\epsilon_{[2,3]}$  are measured in the range  $2\text{--}3 \times 10^{-5} M$ , path length 1 cm.  $\epsilon_{[3,3]}$  is measured at  $8 \times 10^{-5} M$ , 1-cm path length.

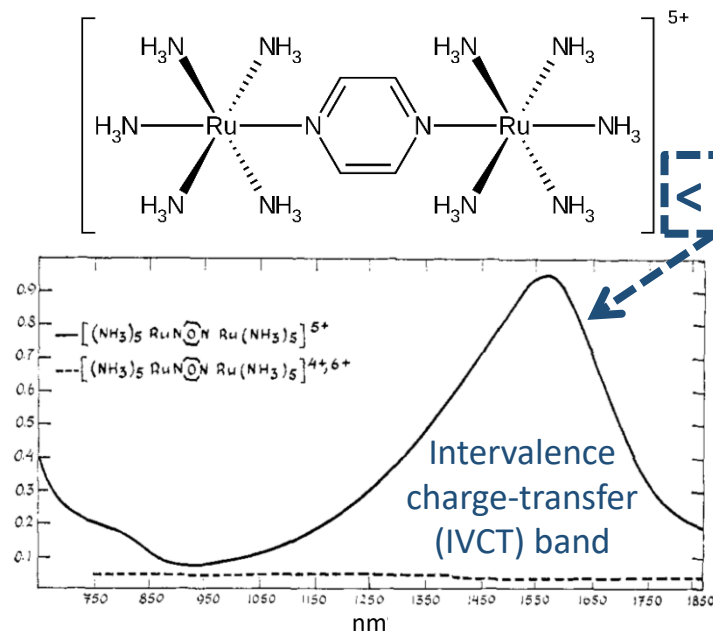


Figure 2. Near-infrared spectrum of [2,3] in  $\text{D}_2\text{O}$ : concentration of [2,3] =  $1.5 \times 10^{-4} M$ ; 1-cm path length. (Dashed line is actually the blank, but accurately indicates the spectra of [2,2] and [3,3] in this range above 750 nm at this concentration level.)

## Taube (1950s–1970s)

inner sphere electron transfer

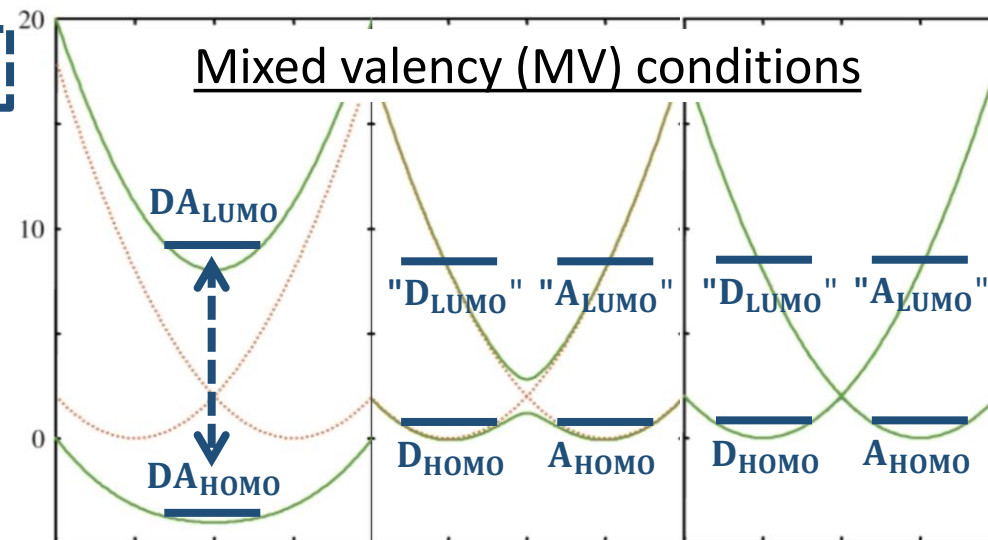
Robin–Day MV classification... **label each below!**

**Class I:** nonadiabatic ( $H_{\text{DA}} \approx 0$ )

**Class II:** adiabatic, localized ( $0 < 2H_{\text{DA}} < \lambda_{\text{AB}}$ )

**Class III:** adiabatic, delocalized ( $2H_{\text{DA}} > \lambda_{\text{AB}}$ )

... so what is  $2H_{\text{DA}}$  for Class III [C–T] $^{5+}$ ?



C. Creutz & H. Taube, *J. Am. Chem. Soc.*, **1969**, *91*, 3988–3989

B. S. Brunshwig, C. Creutz & N. Sutin, *Chem. Soc. Rev.*, **2002**, *31*, 168–184



# Huang–Rhys Factor

## Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{kT}\right)$$

$$= \nu_{\text{n}}(r) \kappa_{\text{el}}(r) \kappa_{\text{n}}(r)$$

$$= \frac{2\pi}{\hbar} \langle \psi'_{\text{el}} | \hat{H} | \psi_{\text{el}} \rangle^2 \langle \psi'_{\text{vib}} | \psi_{\text{vib}} \rangle^2 \delta(E' - E)$$

... separable due to the Born–Oppenheimer approximation

If  $\hbar\omega_j \gg k_{\text{B}}T$ , only  $v_j = 0$  is appreciably populated and

$$\langle \chi_{v_j'} | \chi_{v_j=0} \rangle^2 = \exp(-S_j) \frac{S_j^{v_j'}}{v_j'!} \quad (22)$$

## Fermi's Golden Rule

time-dependent perturbation theory

With one coupled medium- or high-frequency mode (or averaged mode), only the  $v = 0$  vibrational level is appreciably populated at room temperature ( $\hbar\omega \gg k_{\text{B}}T$ ), and<sup>8,43,112,115,131</sup>

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \frac{H_{\text{DA}}^2}{(4\pi\lambda_0 RT)^{1/2}} \sum_v \exp(-S) \frac{S^v}{v!} \exp[-[(\Delta G^\circ + v\hbar\omega + \lambda_0)^2/4\lambda_0 RT]] \quad (25)$$

In this limit the coupled vibration does not contribute to the temperature dependence since the only contributing reaction channels originate from  $v = 0$ .

$S_j$  is the electron-vibrational coupling constant, or Huang–Rhys factor:<sup>99,105</sup>

$$S_j = \frac{1}{2} \left( \frac{M_j \omega_j}{\hbar} \right) (\Delta Q_{e,j})^2 \quad (19)$$

$M_j$  is the reduced mass. The physical significance of the vibrational overlap integrals is that they give the extent to which the final and initial states coincide along the normal coordinate.

... we'll stop here, but it can get even messier, of course...

# Today's Critical Guiding Question

*What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species... and uniquely for today, how does it allow us to quantitatively predict kinetic information... for real this time: Part 2?*