# Part 4. VB diagrams

# VB diagrams by Shaik and Pross

- A powerful VB model for rationalizing reactivity :

*J. Am. Chem. Soc.* **1981**, *103*, 3692–3701

## What Happens to Molecules as They React? A Valence Bond Approach to Reactivity

**Sason S. Shaik**

*Contribution from the Department of Chemistry, Ben-Gurion University of the Negev, P.O.B. 653, Beer Sheva, 84120, Israel.* *Received June 12, 1980*

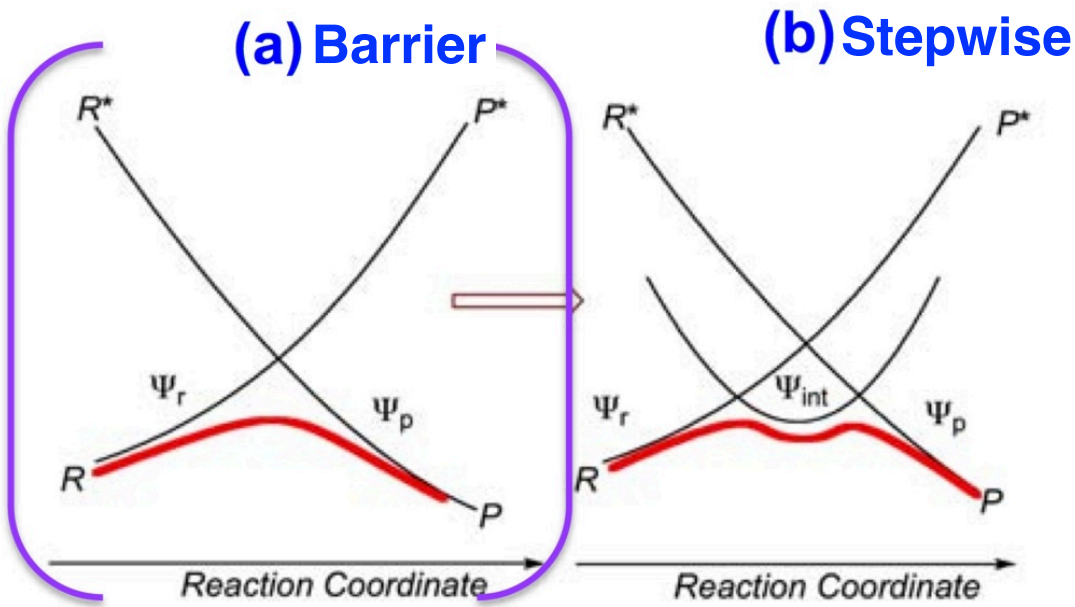
- Developed and applied since then to a huge number of organic chemical reactions, inorganic reactions, clusters and metalloenzymes

- Reviews : https://wiki.lct.jussieu.fr/workshop/index.php/VB_tutorial

# VB diagrams by Shaik and Pross

- A powerful VB model for rationalizing reactivity :

Two archetypal diagrams that describe the major reactivity patterns in **any** chemical reaction :



# Reminders

- Energy expressions from qualitative VB :

**Energy of a determinant with *n pairs of interacting e⁻* : $\sigma 2n\beta S$**

**σ sign : + if attractive, – if repulsion**

- **Bonding energy:**
- **Pauli Repulsion in VB Theory:**

**Elementary Repulsion**

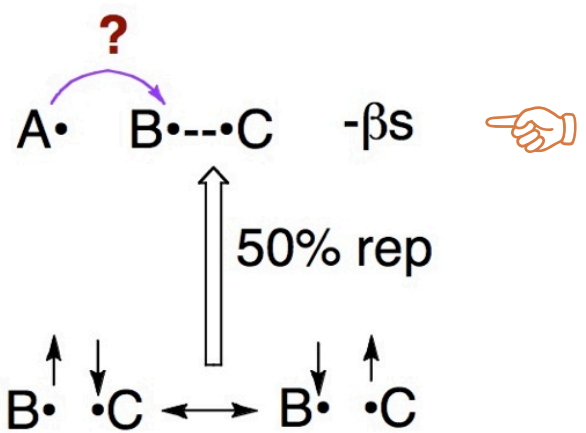
A: :B -2βs >0

A: •B -2βs

A: :B -4βs

A•——• B E = 2βS <0

**Nonbonded Interactions**

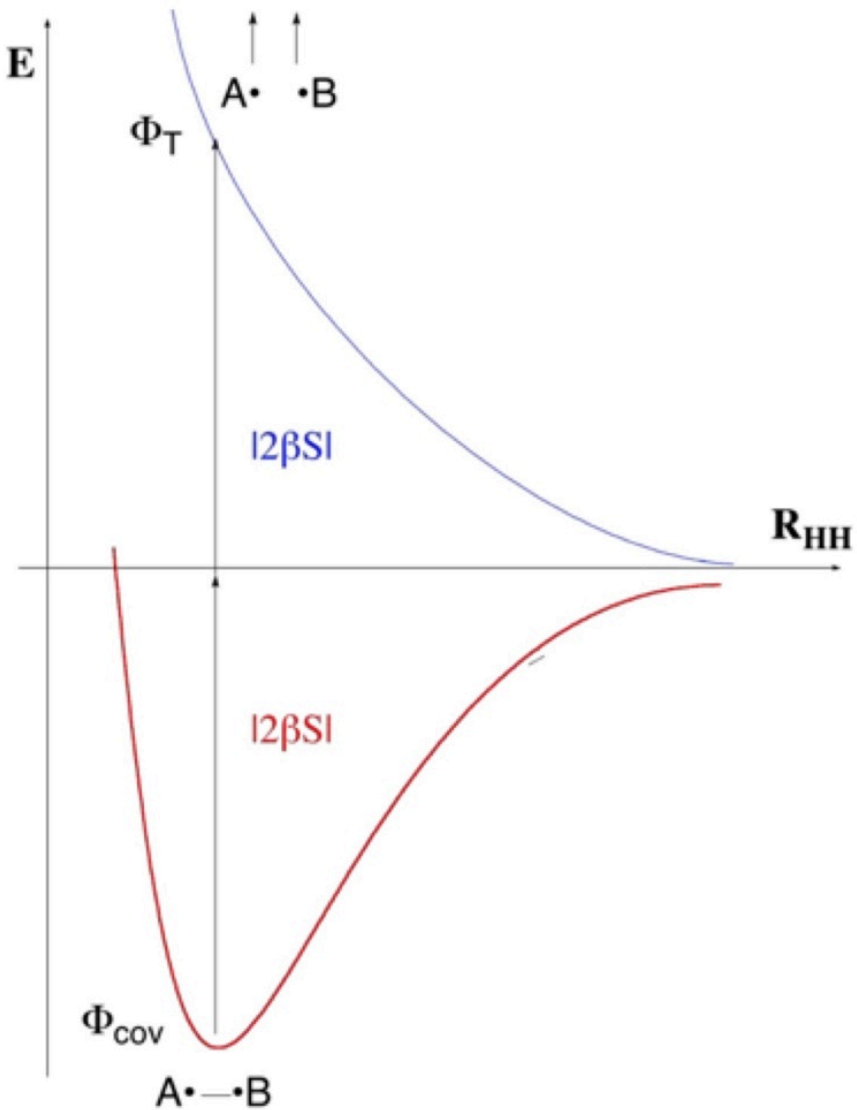


# Reminders

- Singlet-triplet gap :

- Lecture 1 :

**$\Delta E_{ST} \approx 2De$**

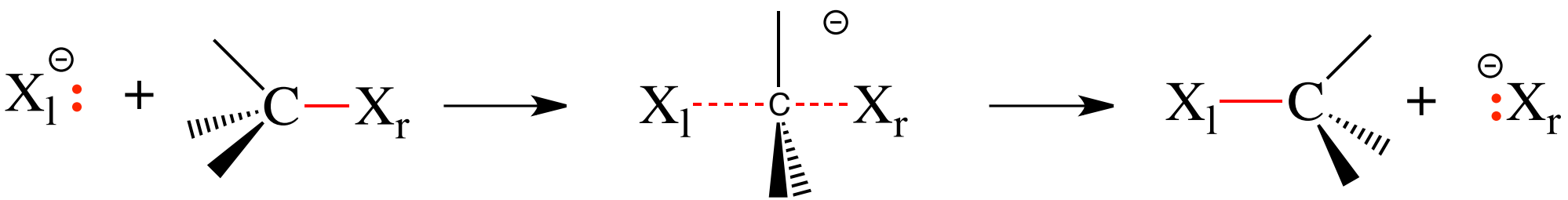



- A more accurate relation :

$$\frac{3}{4}\Delta E_{ST} \approx 2D_e$$

# Principles

- VB diagram for the $S_N2$ reaction :



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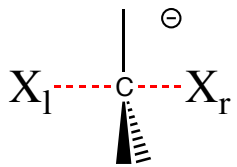
- VB diagram for the $S_N2$ reaction : 



$$\Psi_R \propto \left| x_l \overline{x_l} (c \overline{x_r} + x_r \overline{c}) \right|$$

$$\Psi_R = X:^- + (R_3C\bullet\!-\!\bullet X) \xrightarrow{+2\beta S}$$

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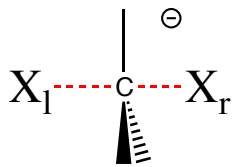


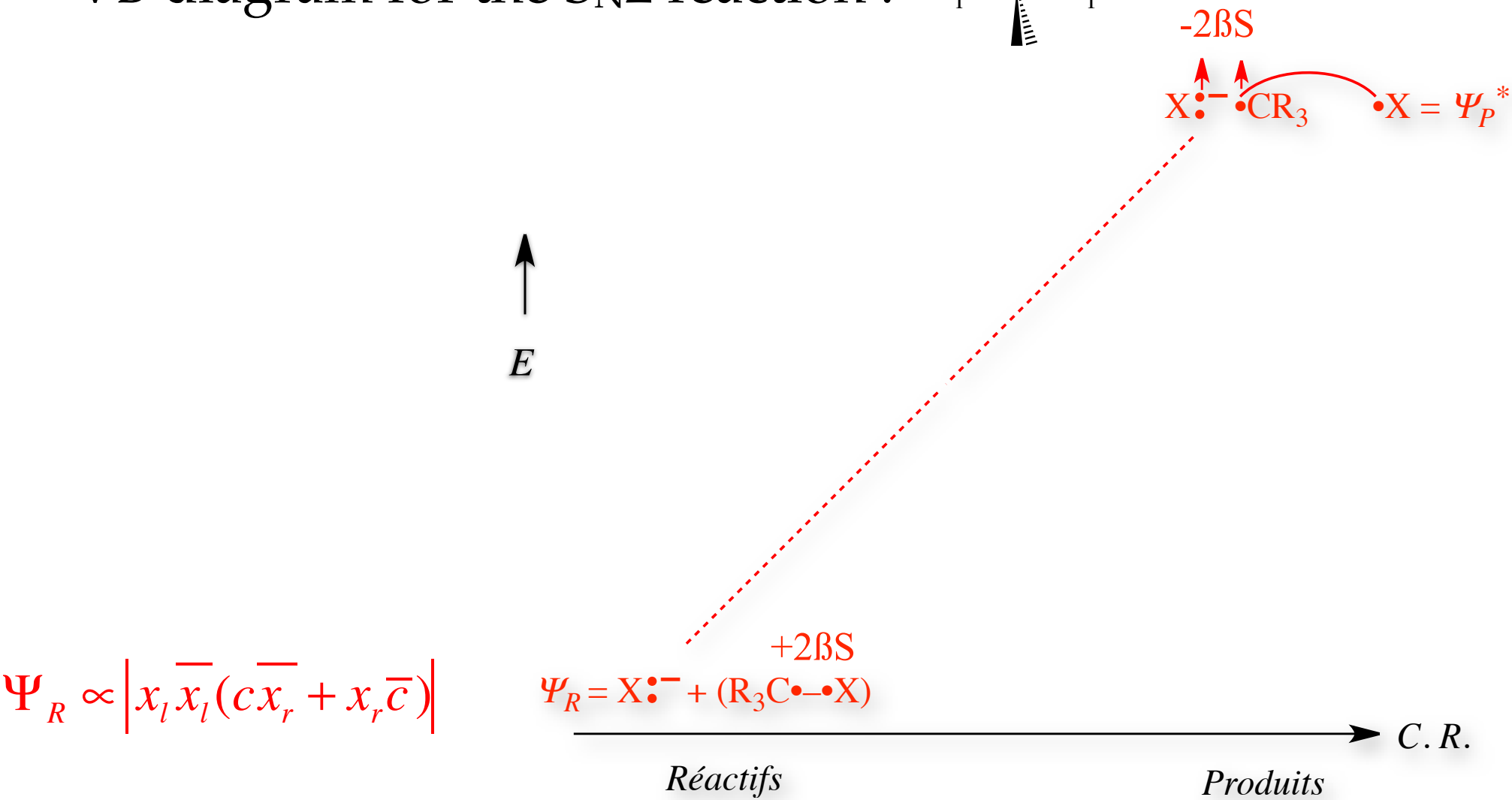


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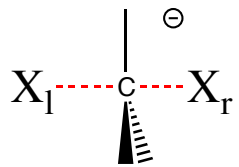


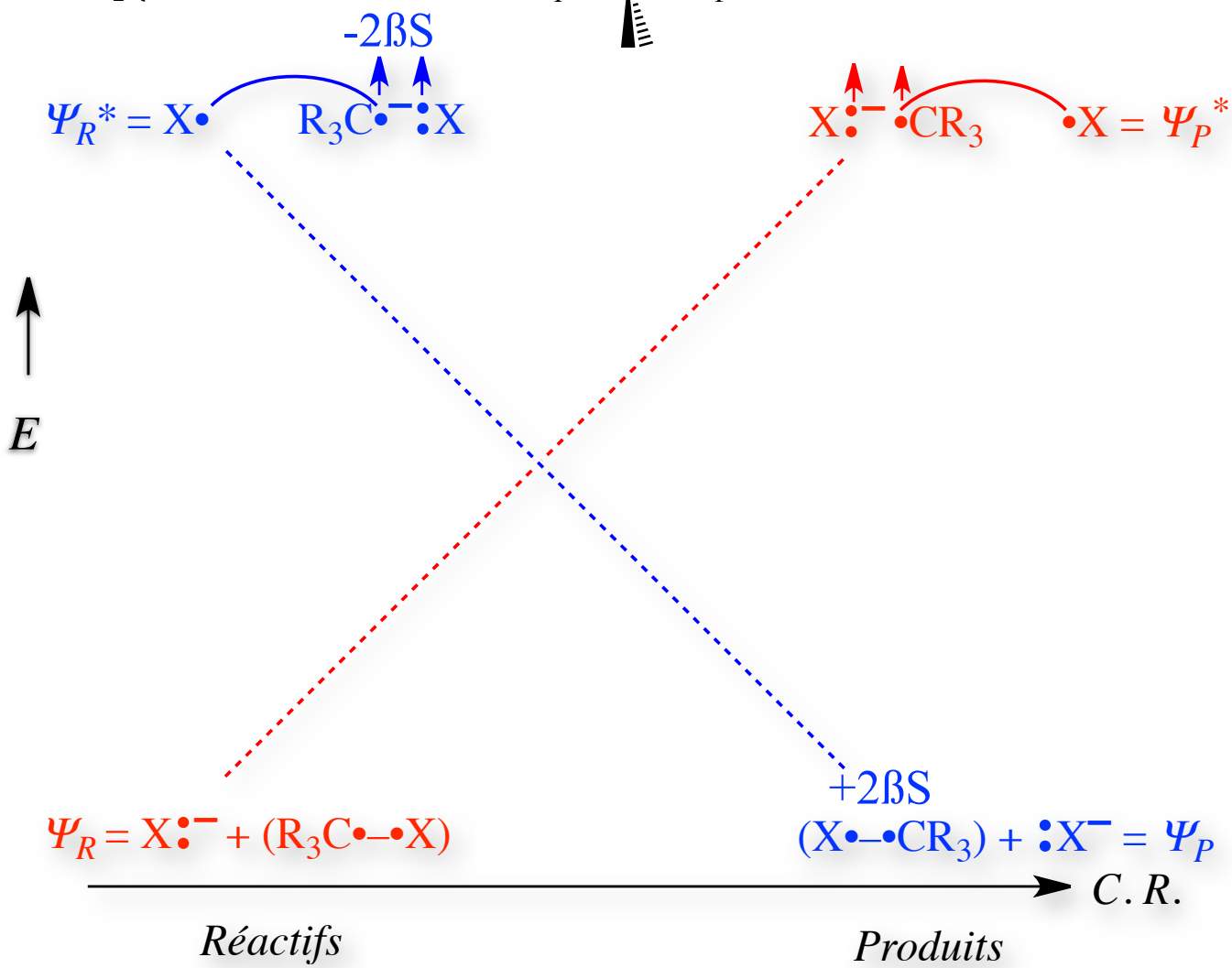


$$\Psi_P \propto \left| (c\overline{x_l} + x_l\overline{c})x_r\overline{x_r} \right|$$

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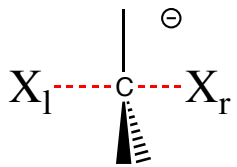


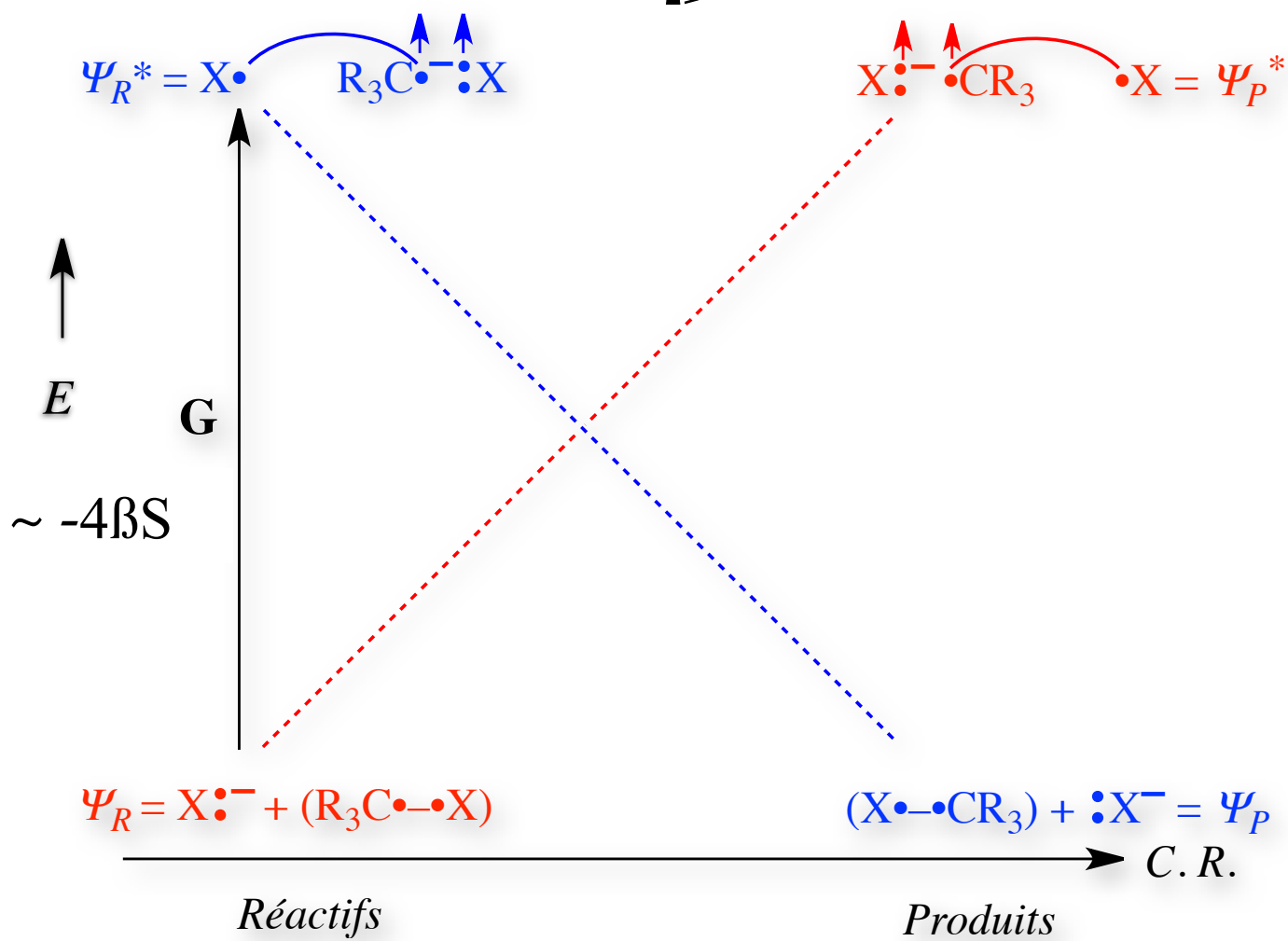

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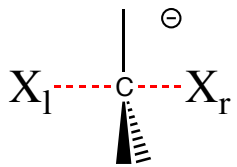


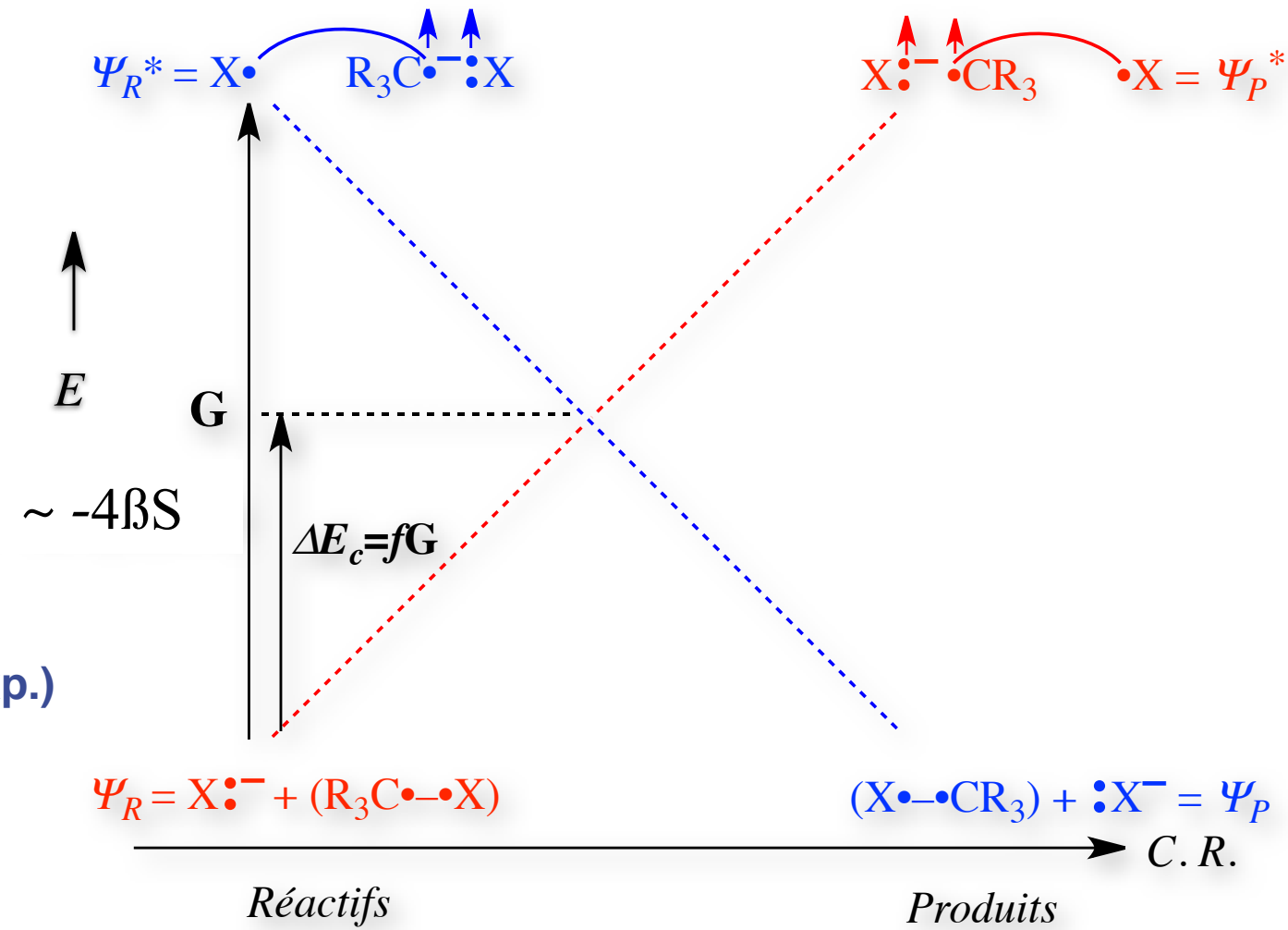


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**f : curvature factor**

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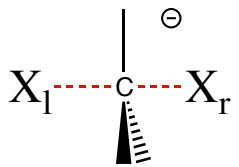
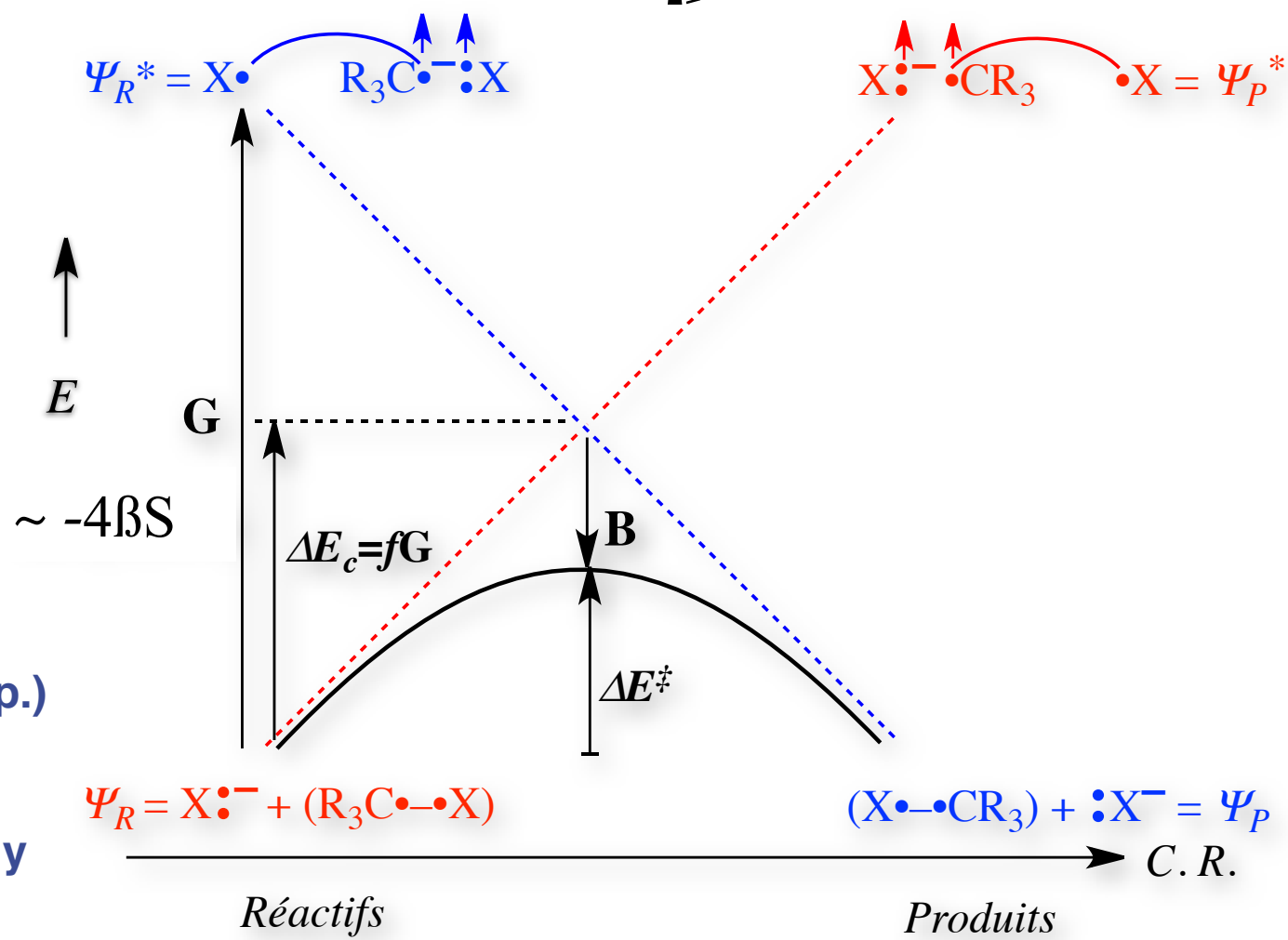



$$\Delta E^{\neq} = f\,G - B$$




**G : reactants' property (exp.)**

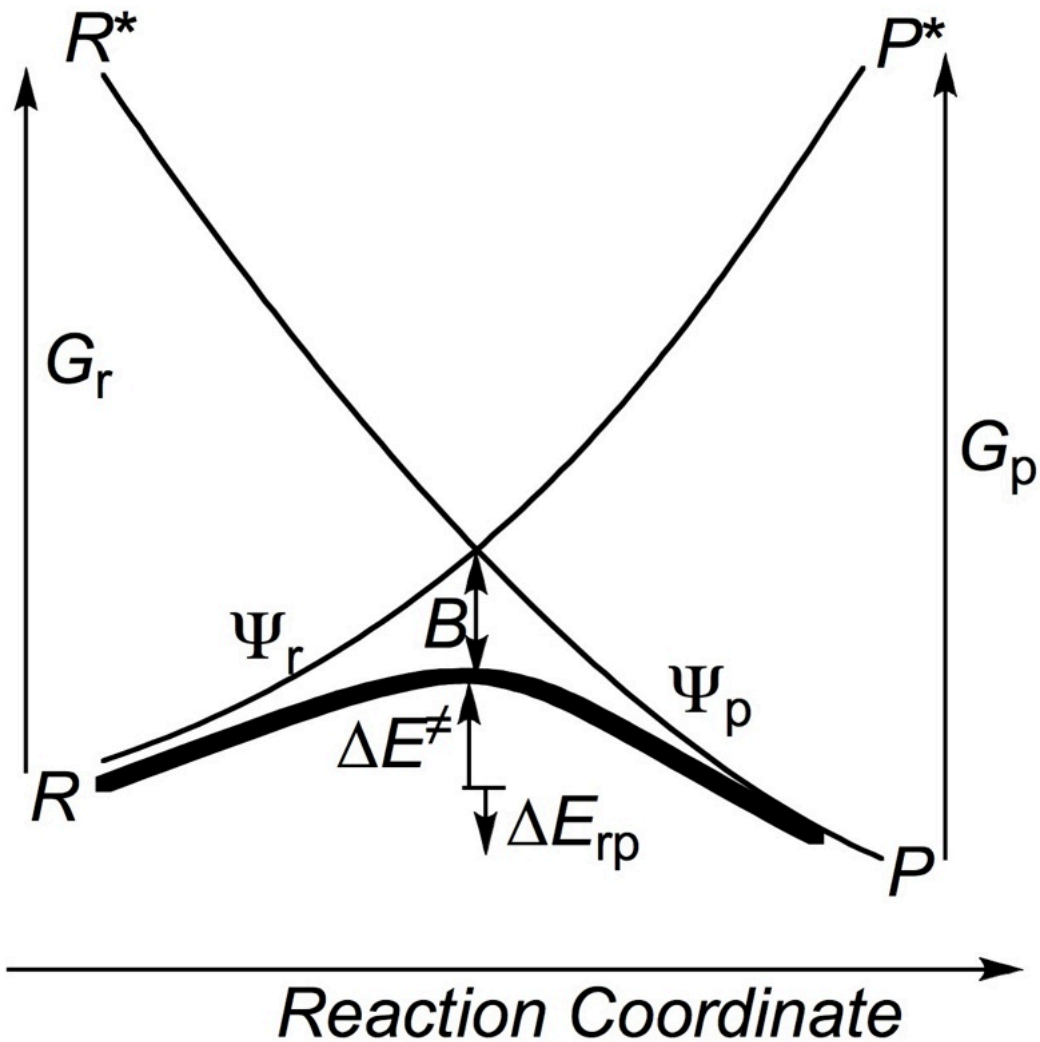
**f : curvature factor**

**B : resonance energy**

# Principles

- Extended formula for the two-state diagrams :

$$\Delta E^{\ddagger} \approx f_0 G_0 - B + 0.5\,\Delta E_{RP} + 0.5\,\frac{\Delta E_{RP}^2}{G_0}$$



# Principles

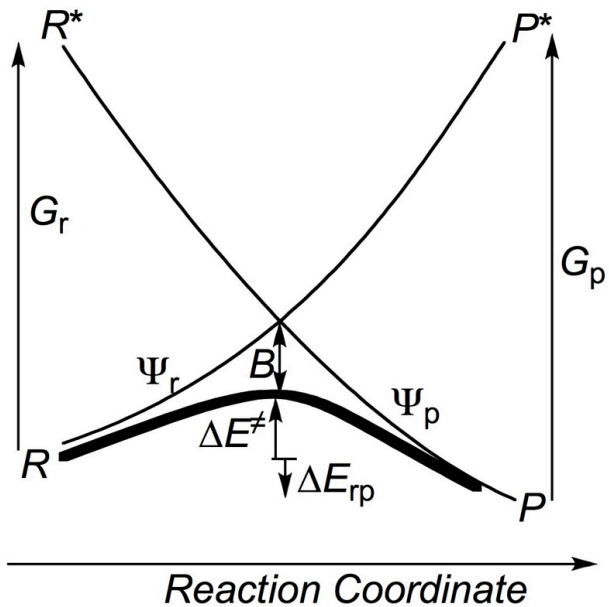
- Basic ingredients of the VB diagrams :

  - **G : promotion energy** : R→R* is an excited diabatic state which prepare the reactants ground state for the bonding changes from R to P.

  - ***f*** **:** measure the **intrinsic «smoothness»** of the electronic structure change in R and P

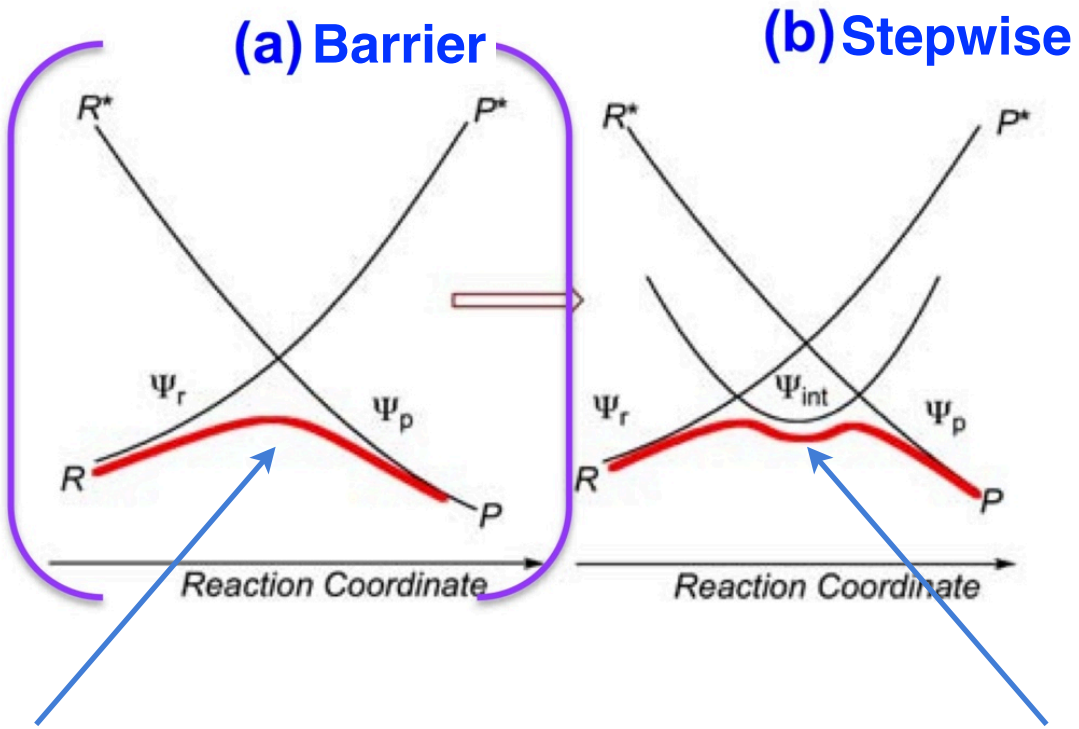
  ⇒ *f*G : gauges the total deformation and repulsive interactions R have to experience to achieve resonance with P

  - **B : resonance energy** of the TS due to VB mixing at the crossing point



# Principles

- Two-state (VBSCD) vs. multi-state diagrams (VBCMD) :




R and P mix to form the barrier and the TS for an elementary process

The intermediate has a different electronic structure than R and P («internal catalysis»)

# G expressions

- How to derive quantitative expressions for G ?

The promoted states involve two elementary excitations, depending on whether there are **changes in the oxidations states** of fragments or not

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- How do I know if there is a change in oxydation state ?

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2) count the **number of electrons on each fragment**

3) **does this number change** during reaction ? → **NO** : **no change** of ox. state

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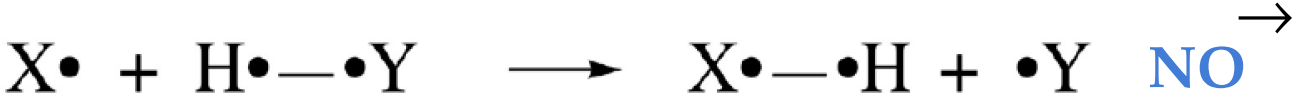



NO

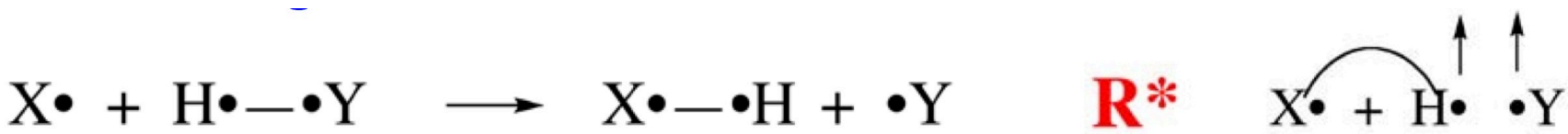

YES

# G expressions

- **Rule 1** : no change in oxydation state :
  - What happens during R→R* promotion :

1) Bonds which are broken are decoupled to their triplet state in R*

2) Electrons are paired anew as in P

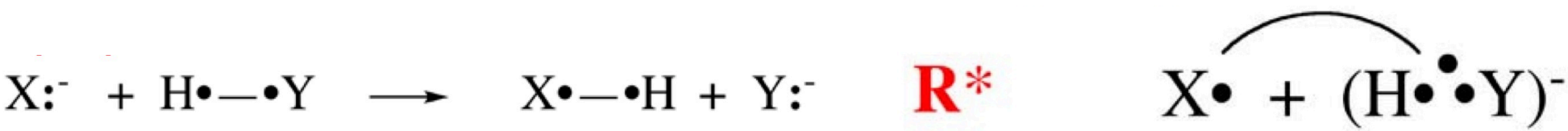



$$\Rightarrow G_r \approx \Delta E(S \rightarrow T)$$

# G expressions

- **Rule 2** : change in the oxydation state :
  - What happens during R→R* promotion :

    Charge transfer from the fragment being oxydized (lose 1e⁻) to the fragment being reduced (gain 1e⁻)




$$\Rightarrow G_r \approx IP(X:) - EA(H-Y)$$

# G expressions

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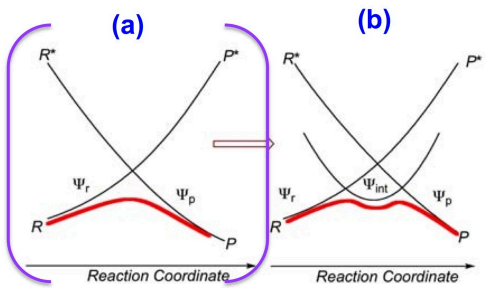
- **Rule 2** : change in the oxydation state :

$$\Rightarrow G_r \approx IP(X:) - EA(H - Y)$$

- How to get ΔE(S→T), IP, EA ?
  - Accurate computations (not specially VB !)
  - From experiments

# In short

- Two type of diagrams for all reactions




- Three main parameters (G, f, B) to express the barrier

$$\Delta E^{\neq} = f\,G - B$$

- Two rules for expressing G

NO $\Rightarrow G_r \approx \Delta E(S \rightarrow T)$

YES $\Rightarrow G_r \approx IP(X:) - EA(H - Y)$

# Illustrations

- Anion/Cation recombination
- Nucleophilic addition
- $X_3$ radical exchange reactions
- Allowed/forbidden cycloadditions
- SN2(C) vs. SN2(Si) - Origin of hypercoordination
- XHX vs HXH radical exchange reactions
- A single electron may change everything

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# Illustrations

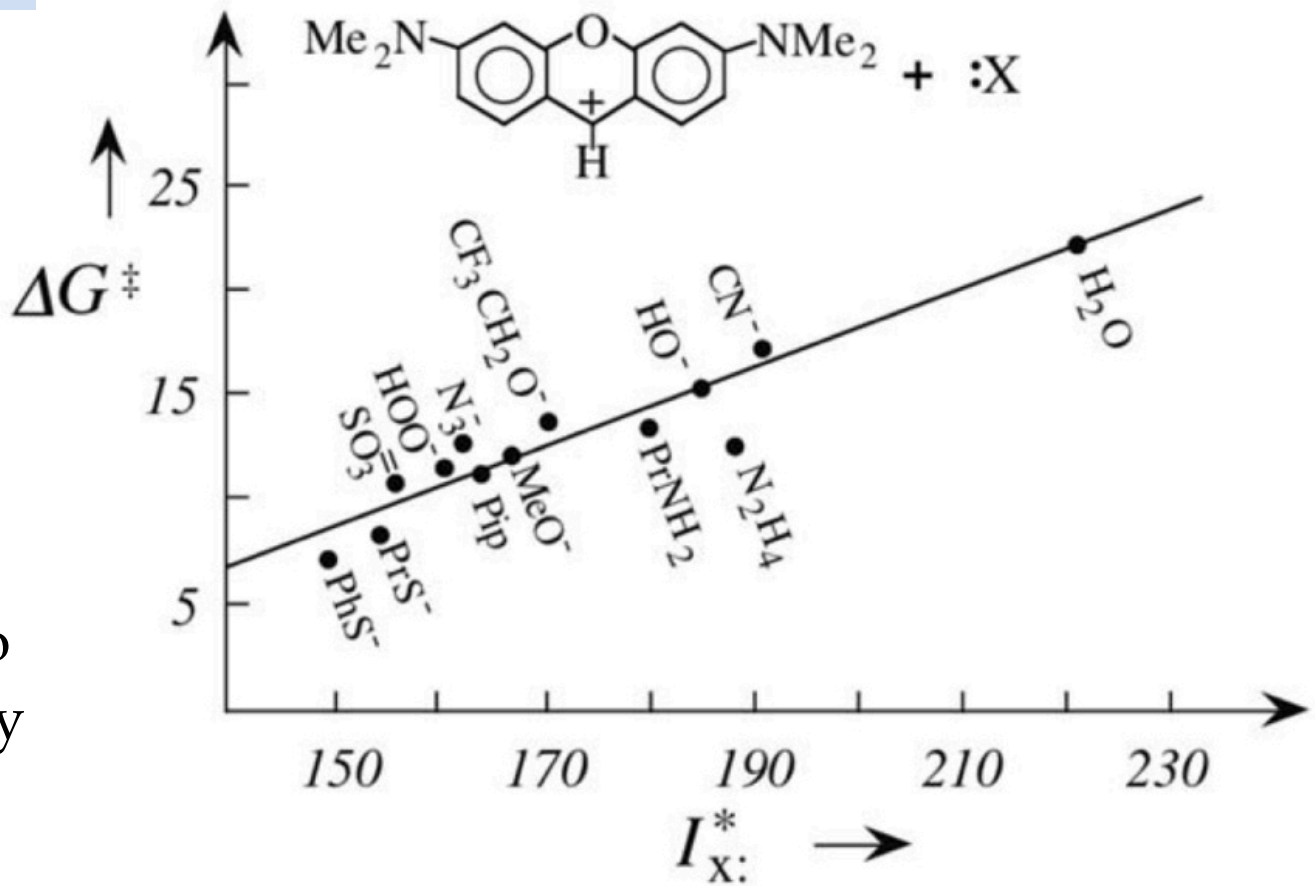
- Anion/Cation recombination : **$X:^- + R^+ \rightarrow X\text{-}R$**

Rule 2 : $G_r \approx IP(X^- :) - EA(R^+)$

In this serie the carbocation

$R^+$ is common

➡ VB diagram bring order to the concept of nucleophilicity



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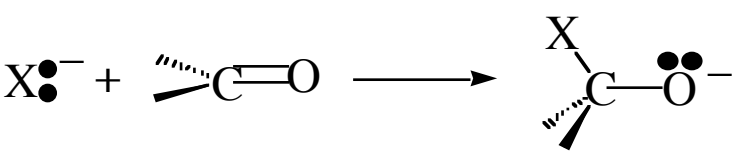

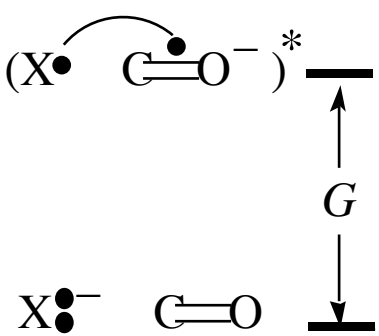


$G = I^*_{X:} - A^*_{C=O}$

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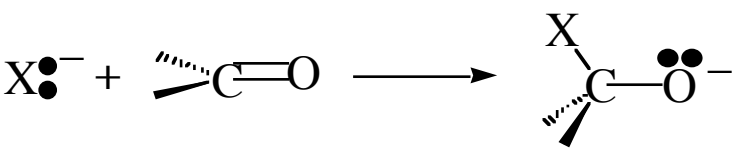

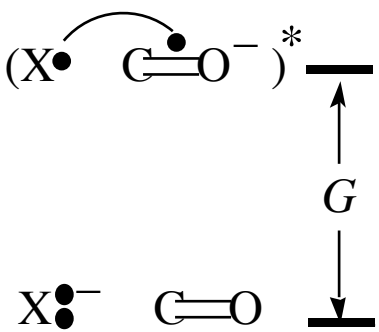


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**First set : localized**

**$X:^-$ = $F^-$, $CN^-$, $HO^-$, $HOO^-$**

**$CF_3CH_2O^-$, $CH_3O^-$,**

$\Delta E^{\neq} = f_1(IP(X^-)) + cte$

**Second set : delocalized**

**$PhS^-$, $PhO^-$, $N_3^-$, $NO_2^-$, $AcO^-$**

$\Delta E^{\neq} = f_2(IP(X^-)) + cte$

$f_2 > f_1$

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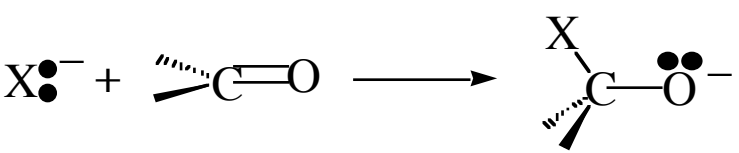

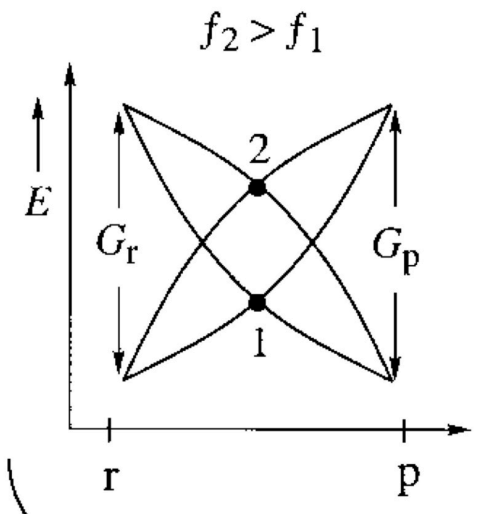


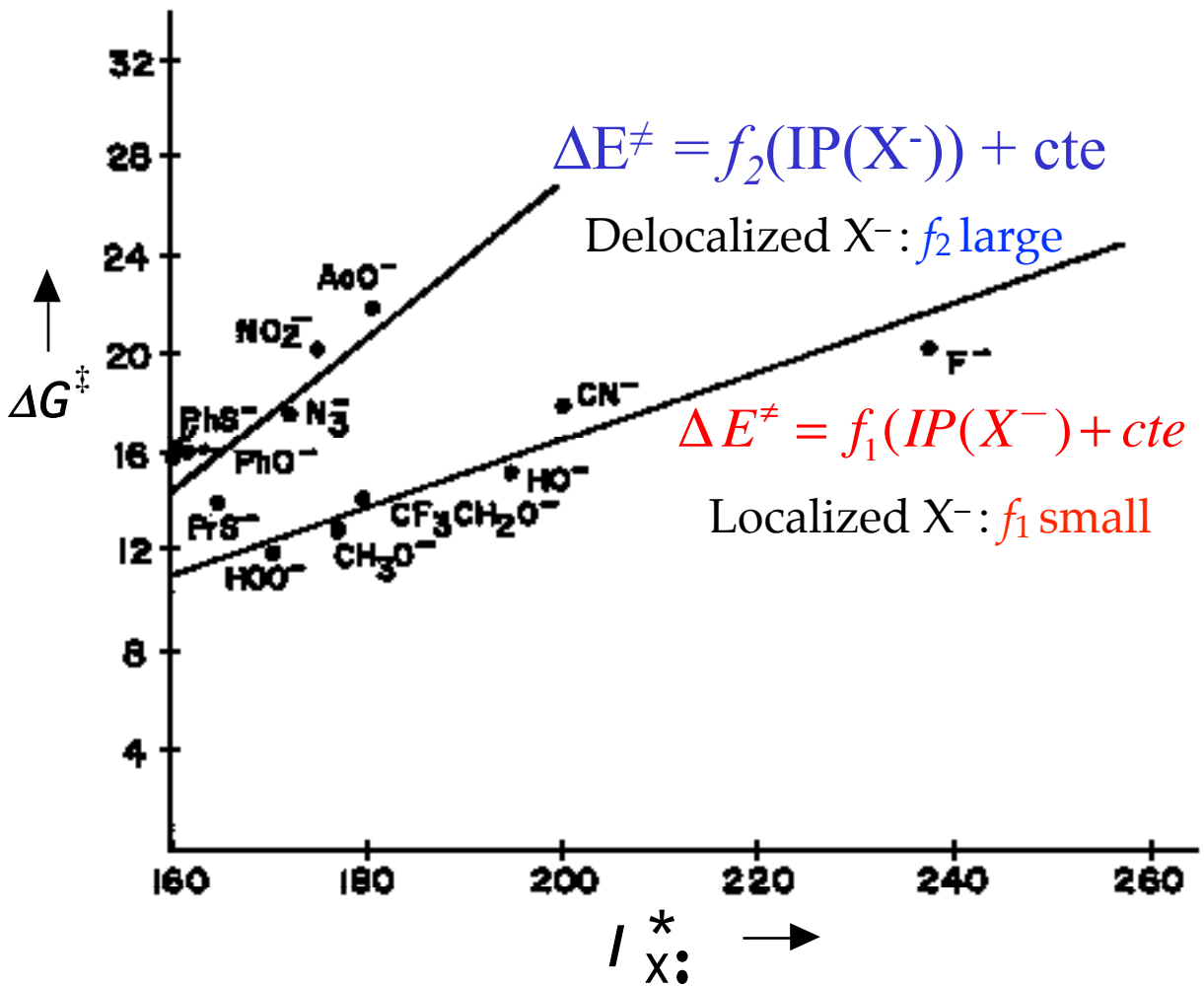

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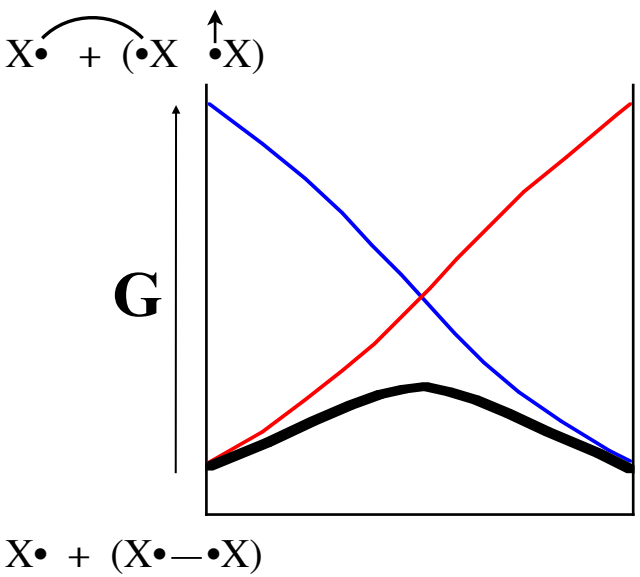
- Radical exchange reactions

**Stability or unstability of $X_3$• clusters** (X= H, F, Cl, Br, I, Li, Na, etc.)

**X• + X-X → [X--X--X]• → X–X + X•**

$$\text{Rule 1}: \Rightarrow G \approx \Delta E_{ST}(X-X) \propto 2D_e$$




Strong bonds ($H_3$):
Large barrier

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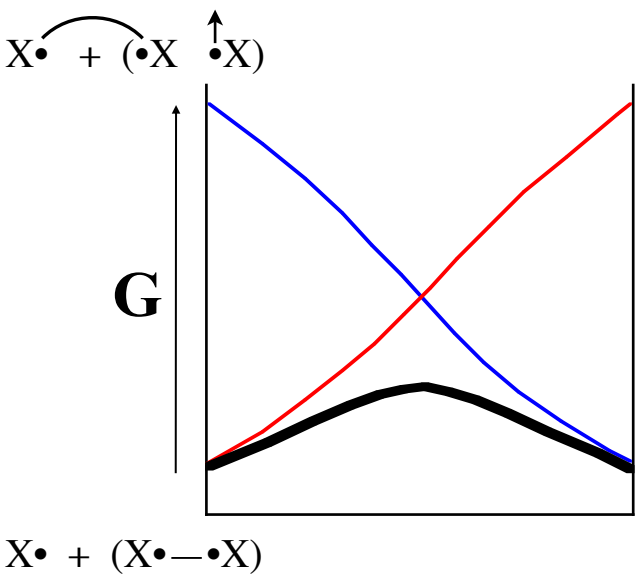


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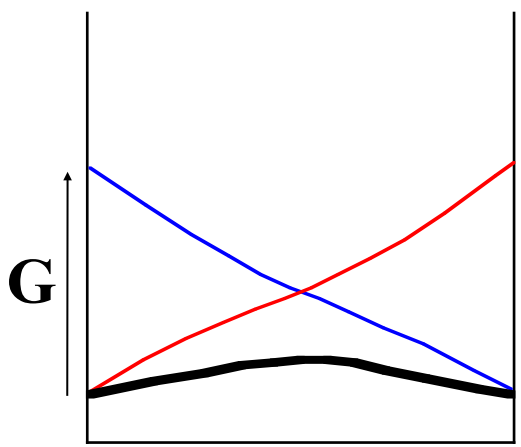


Weaker bonds ($Cl_3$):
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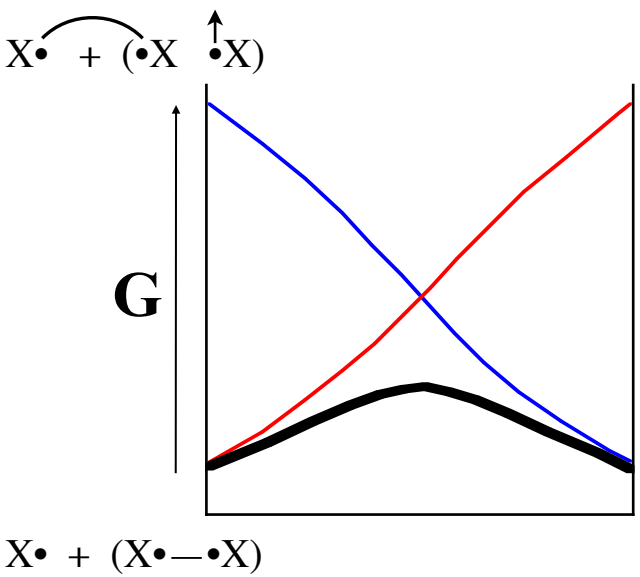


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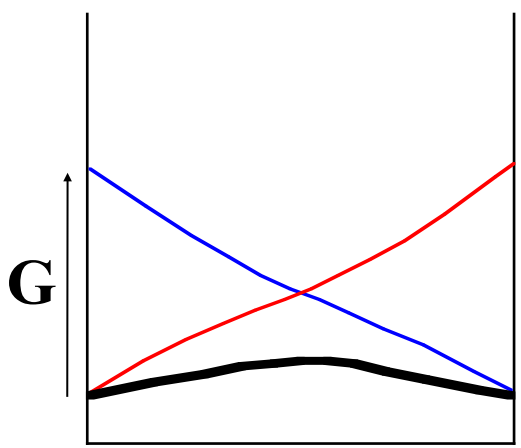


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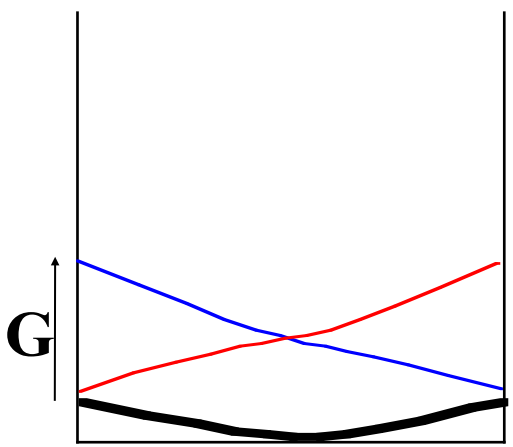


Weak bonds ($Li_3$):
Stable cluster

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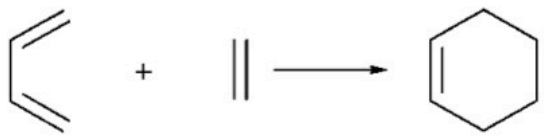

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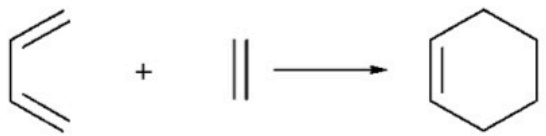

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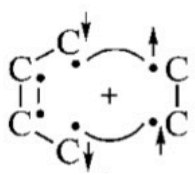
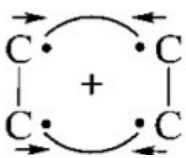
[2+2]

R* 

R* 

Rule 1 : $G = \Delta E_{ST}(D) + \Delta E_{ST}(O)$

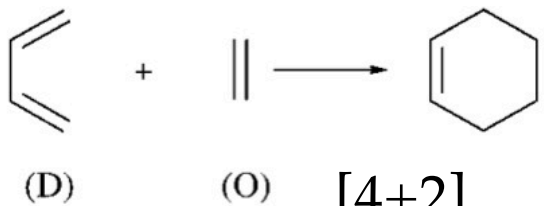
$G = 2\Delta E_{ST}(O)$

with : $\Delta E_{ST}(O) > \Delta E_{ST}(D)$

➡ G lower for [4+2] cycloaddition

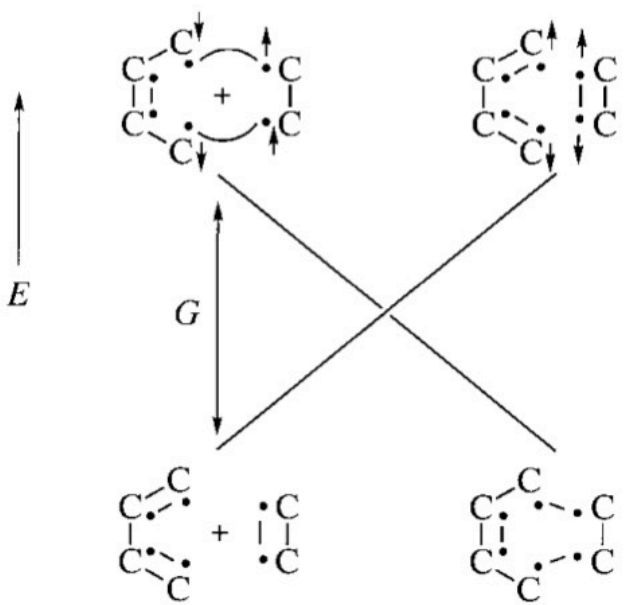
# Illustrations

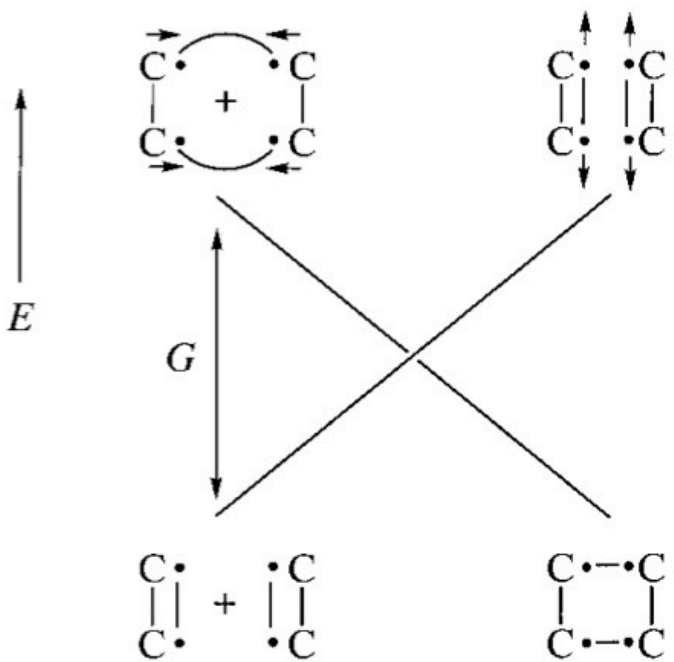
- Allowed / forbidden cycloadditions



(D) (O) [4+2]

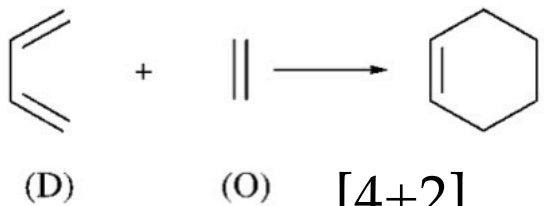
[2+2]



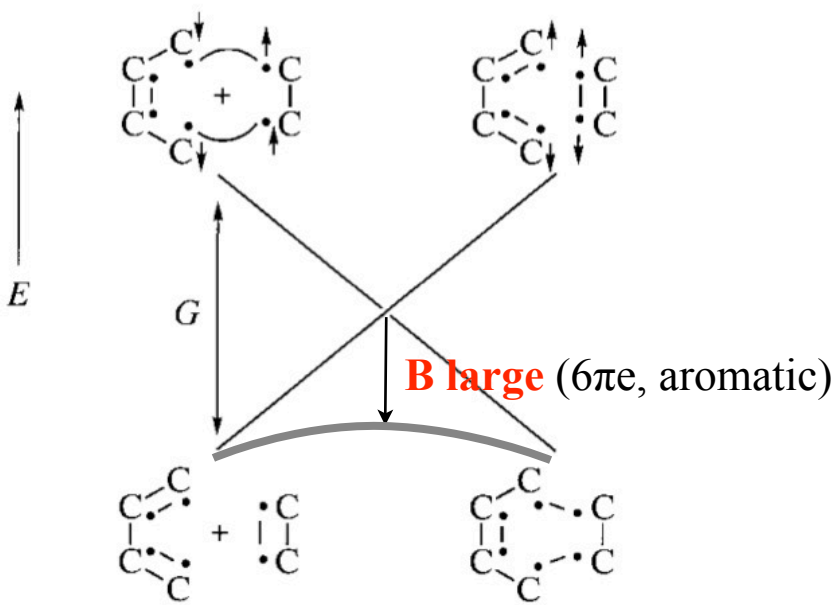
# Illustrations

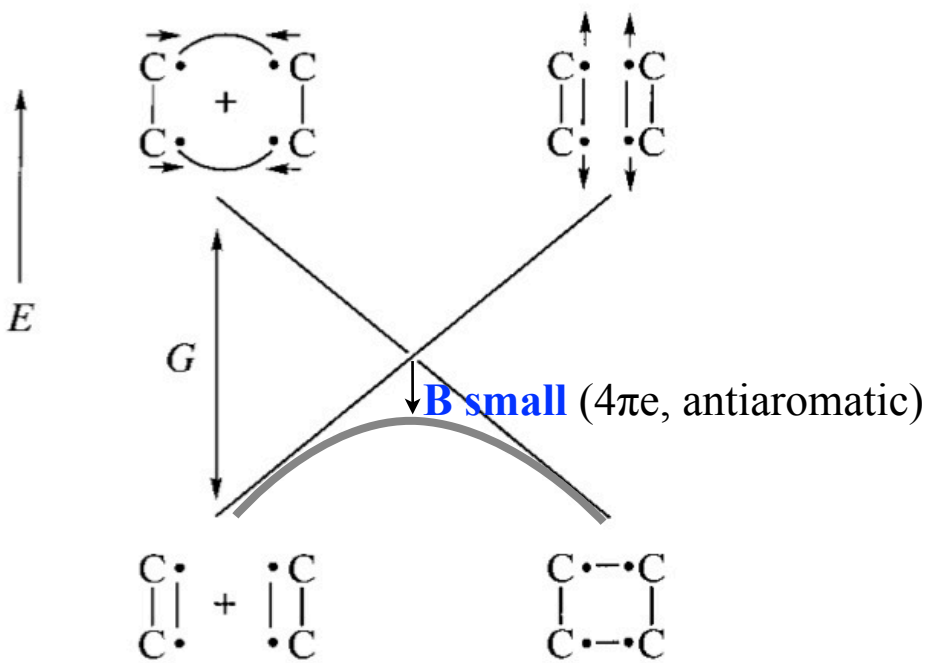
- Allowed / forbidden cycloadditions




[4+2]

[2+2]



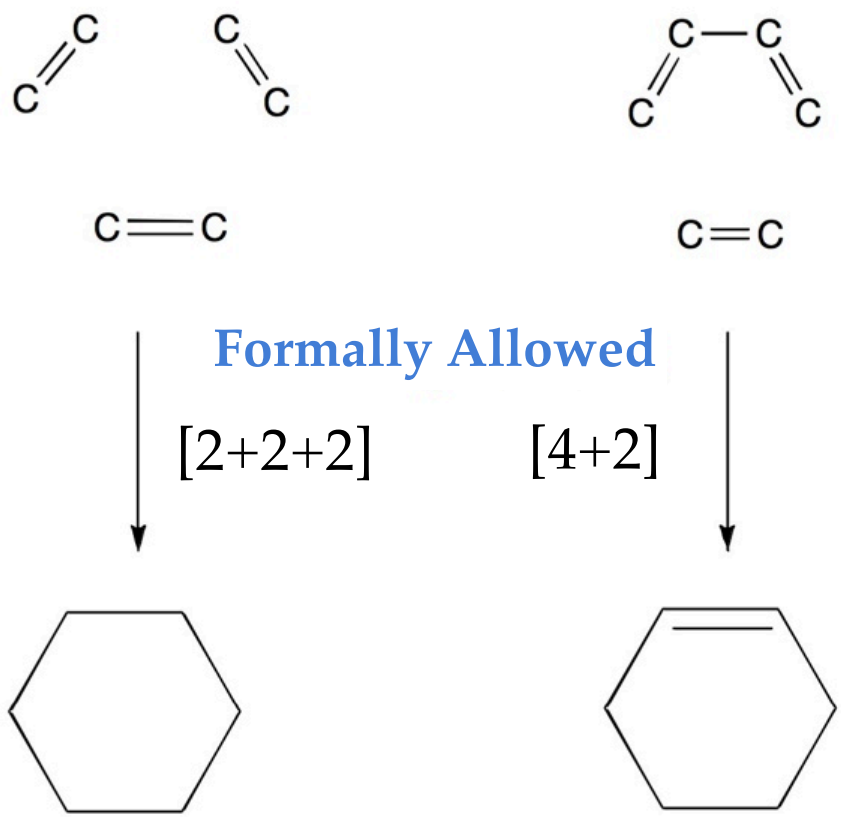




➡ G lower and B larger for [4+2] cycloaddition

$$\Delta E = fG - B$$

# Illustrations

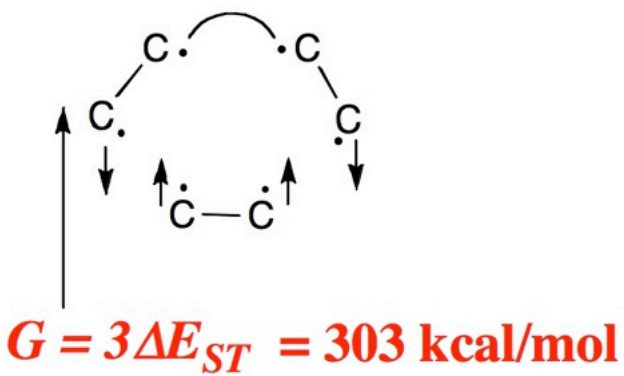
- Allowed / forbidden cycloadditions



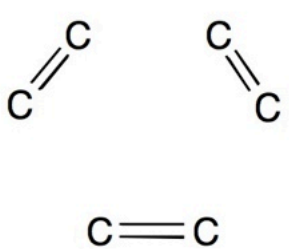

Higher thermodynamic driving but much higher barrier...

# Illustrations

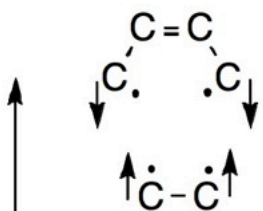
- Allowed / forbidden cycloadditions



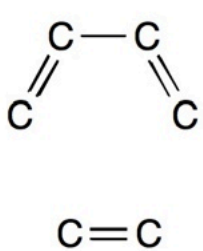
$G = 3\Delta E_{ST} = 303$ kcal/mol







$G = \Delta E_{ST}^{(diene)} + \Delta E_{ST}^{(ethene)} = 179$ kcal/mol



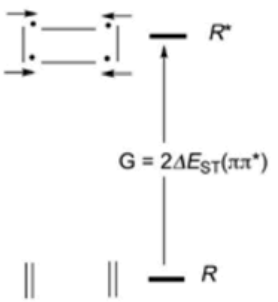


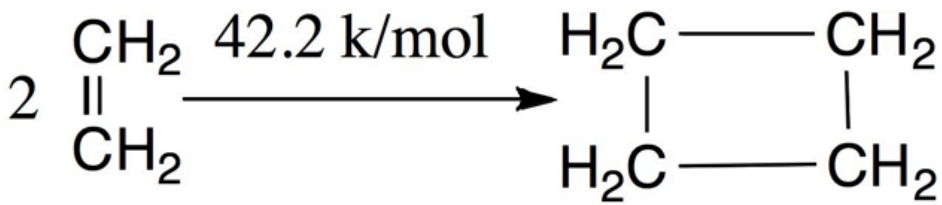
➡ G much higher for [2+2+2] cycloaddition

# Illustrations

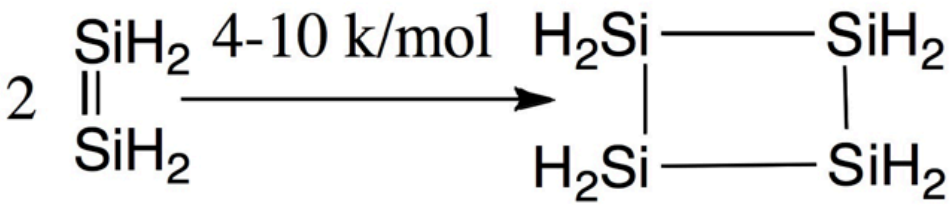
- Allowed / forbidden cycloadditions
  - G involve S→T decoupling of the two π bonds :

    **Formally Forbiden**




$G_C = 2\Delta E_{ST}(\pi\pi^*) = 202$ kcal/mol



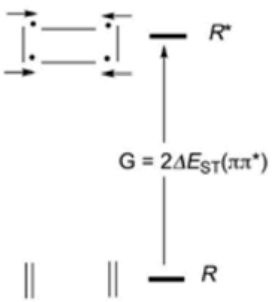

$G_{Si} = 2\Delta E_{ST}(\pi\pi^*) = 80$ kcal/mol

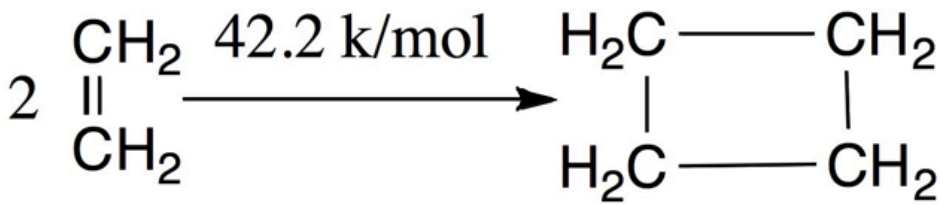
- Estimation using the formula ($\Delta E^{\neq} = fG - B$) and $f$=0.3 (typical value) lead to a barrier difference of 40 kcal.mol$^{-1}$ for Si vs C : not bad !

# Illustrations

- Allowed / forbidden cycloadditions
  - G involve S→T decoupling of the two π bonds :

    **Formally Forbiden**

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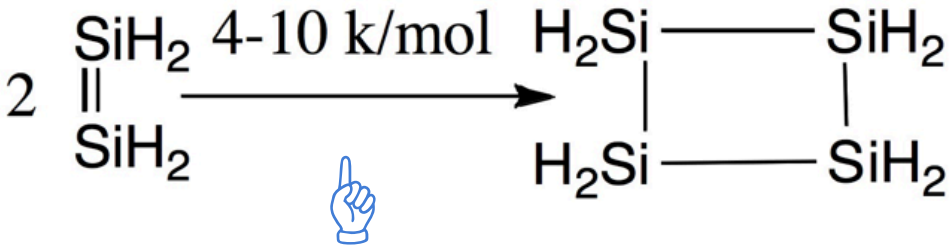



$G_{Si} = 2\Delta E_{ST}(\pi\pi^*)$=80 kcal/mol

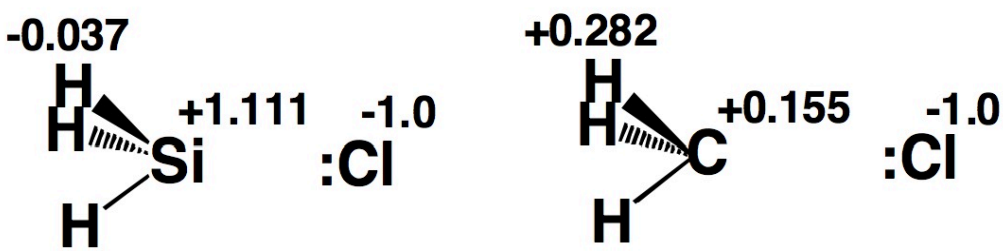
It is even faster than the (formally allowed) Diel-Alder reaction with G=179 kcal.mol$^{-1}$ !

# Illustrations

- Anion/Cation recombination
- Nucleophilic addition
- $X_3$ radical exchange reactions
- Allowed/forbidden cycloadditions
- SN2(C) vs. SN2(Si) - Origin of hypercoordination
- XHX vs HXH radical exchange reactions
- A single electron may change everything

# Illustrations

- SN2(C) vs. SN2(Si) - Origin of hypercoordination :

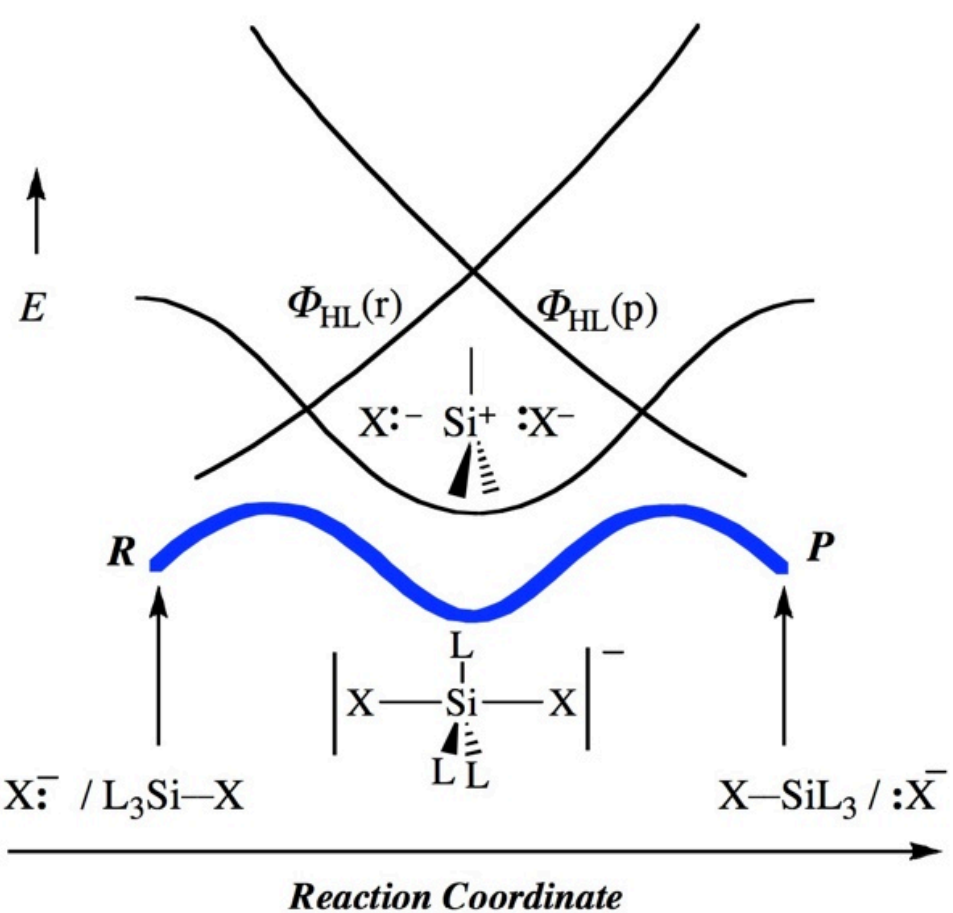


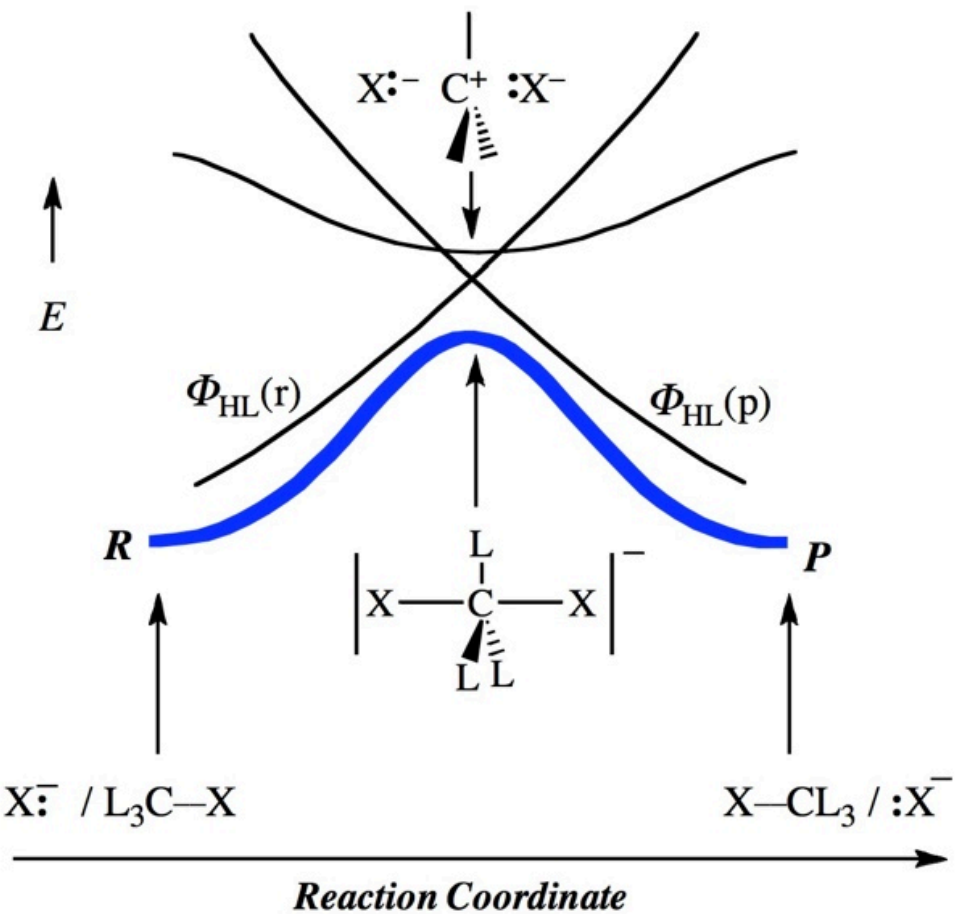

Positive charge localization on Si vs. delocalization on C

⇒ Si small ion allowing close approach of anions and a significant electrostatic stabilization of its ionic structure

# Illustrations

- SN2(C) vs. SN2(Si) - Origin of hypercoordination :



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# Illustrations

- Barrier in radical exchange reactions :

$$X^{\bullet} + H\text{–}X \rightarrow [X\ldots H\ldots X]^{\bullet} \rightarrow X\text{–}H + X^{\bullet}$$

| | $\Delta E^{\neq}$ (kcal/mol) |
|---|---|
| FHF | 20.9 |
| ClHCl | 11.0 |
| BrHBr | 8.0 |

# Illustrations

- Barrier in radical exchange reactions :

$$H^{\bullet} + X\text{–}H \rightarrow [H\ldots X\ldots H]^{\bullet} \rightarrow H\text{–}X + H^{\bullet}$$

| | $\Delta E^{\neq}$ (kcal/mol) |
|---|---|
| HFH | 42.5 |
| HClH | 18.5 |
| HBrH | 12.9 |

# Illustrations

- Barrier in radical exchange reactions :

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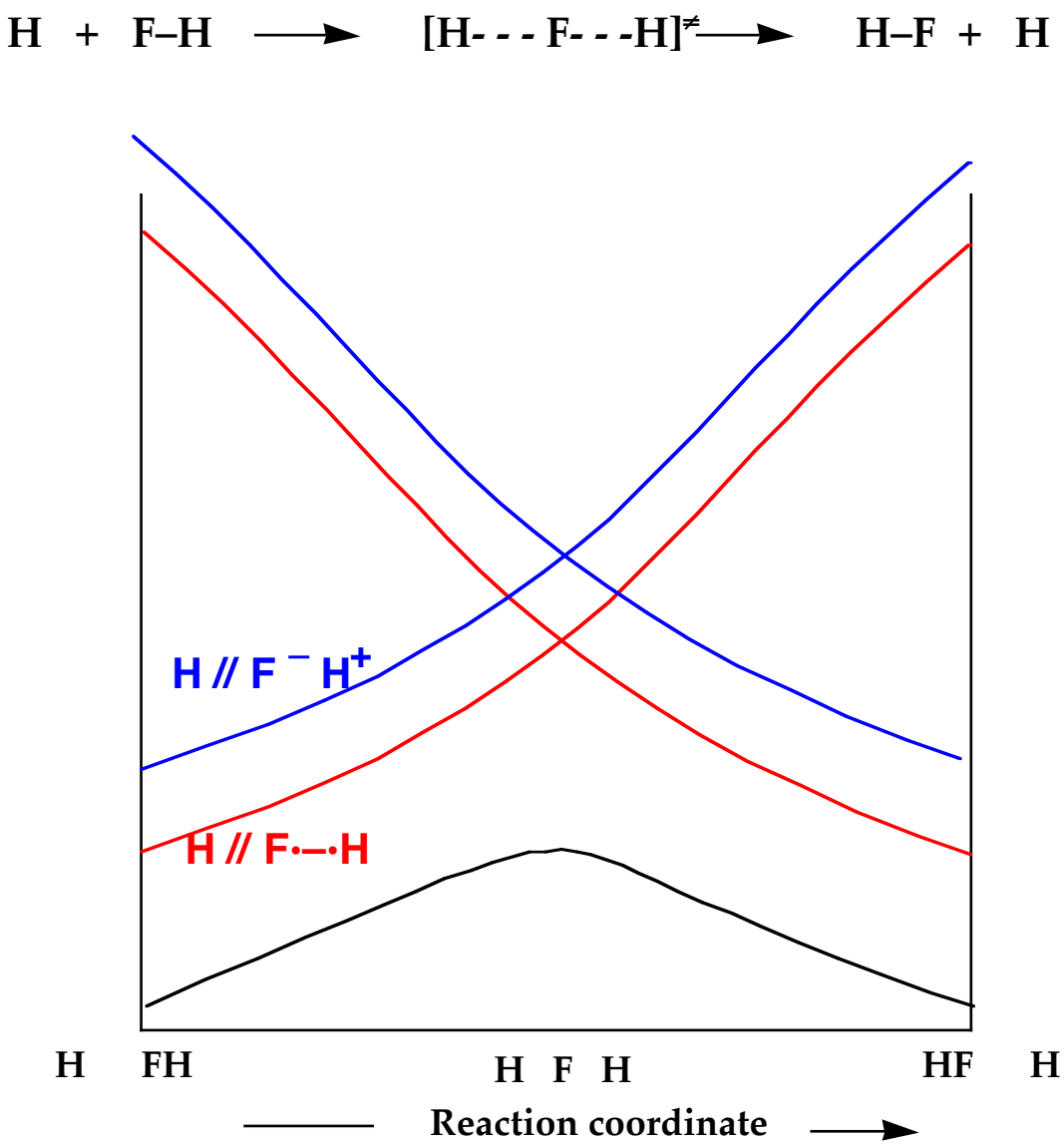
# Illustrations




**VB state-crossing diagrams**

Similar diagrams for FHF reaction...

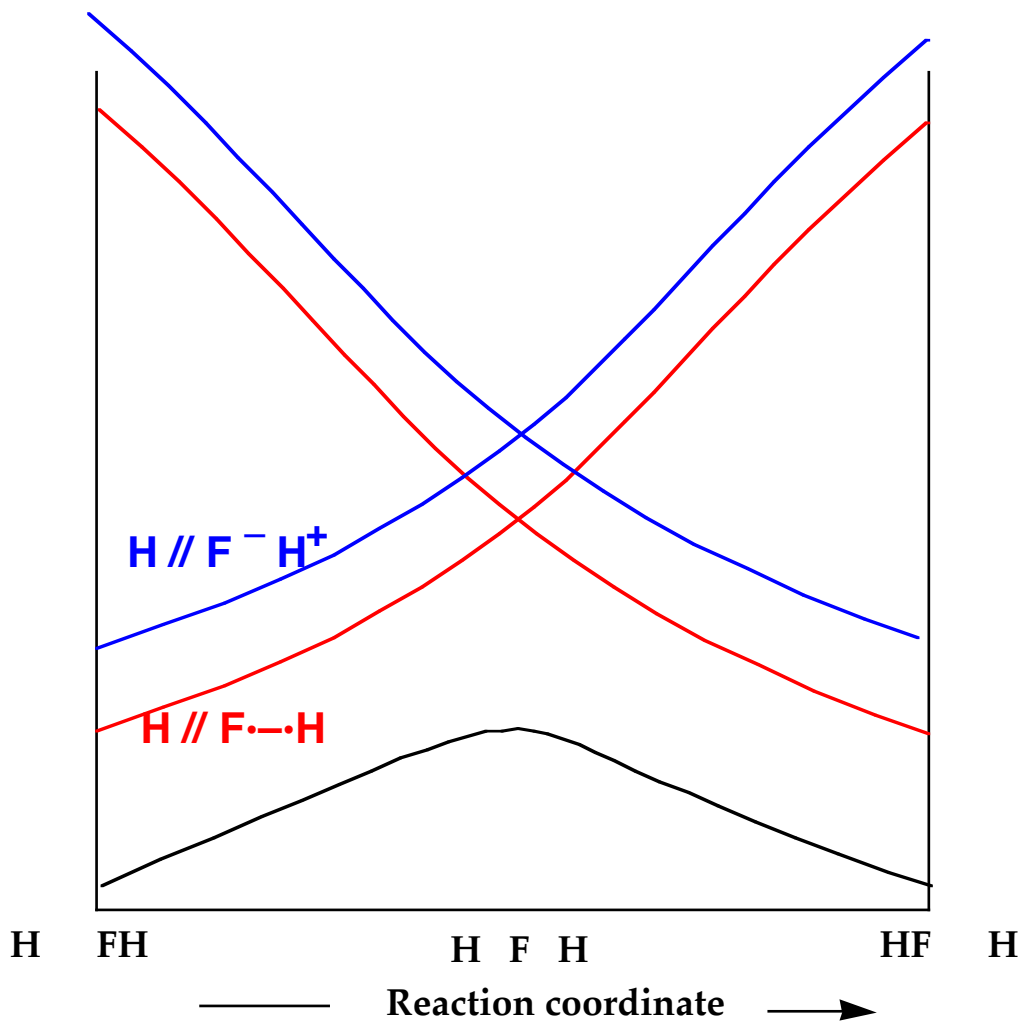
# Illustrations

**VB state-crossing diagrams**

Similar diagrams for FHF reaction...

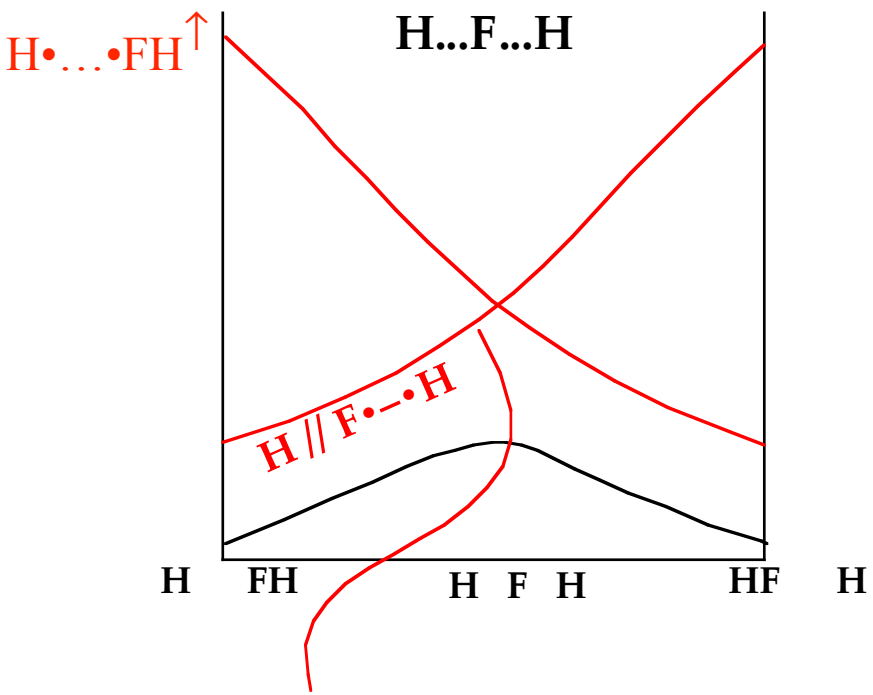
$$G = \Delta E_{ST}(F - H)$$

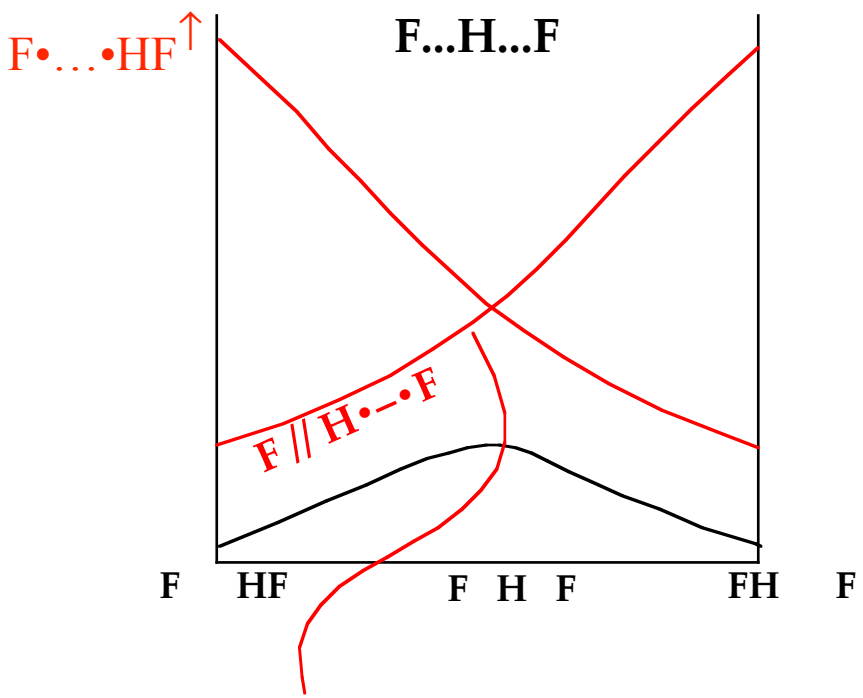
Same G also !



# Illustrations

## The covalent curves

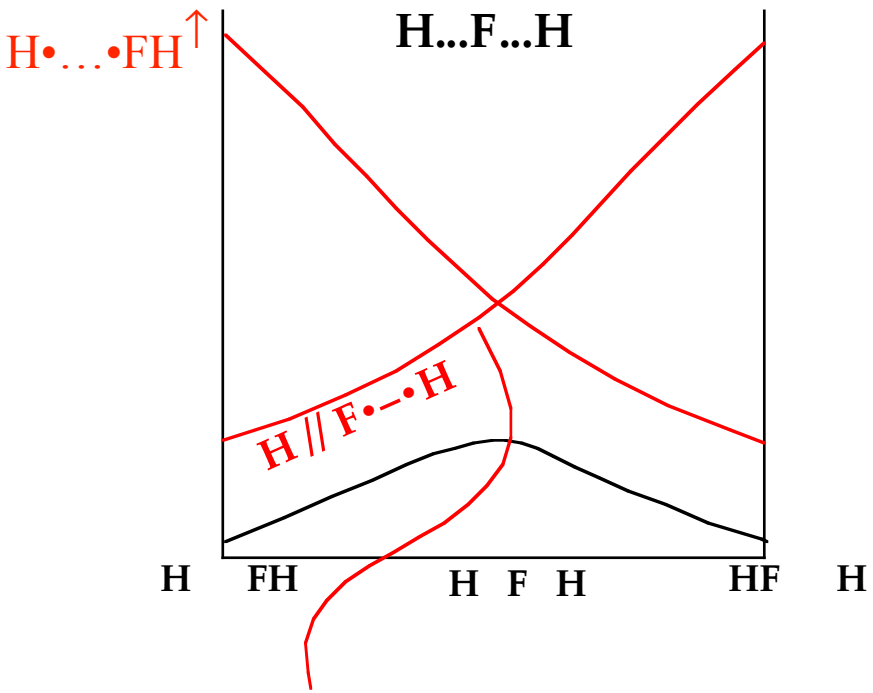


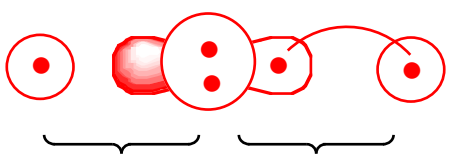

On the basis of covalent structures alone, both reactions should have the same barriers !

# Illustrations

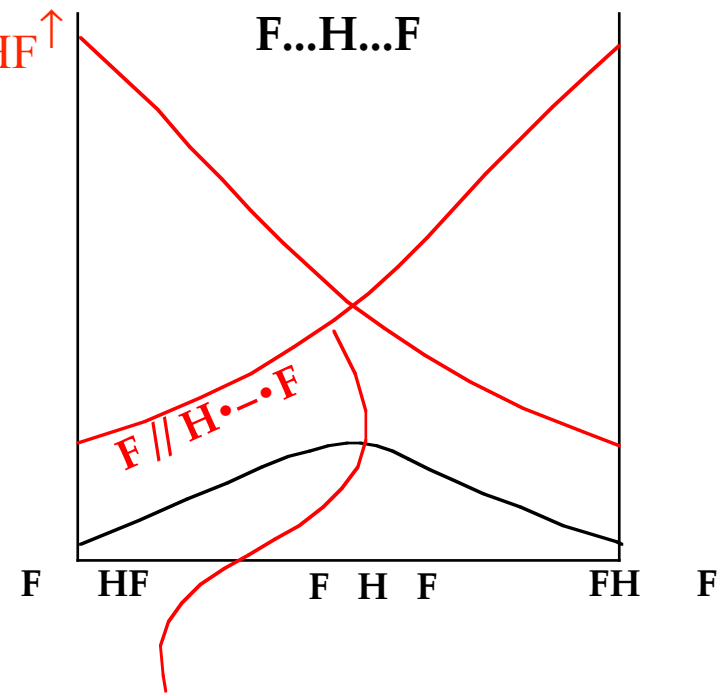
## The covalent curves



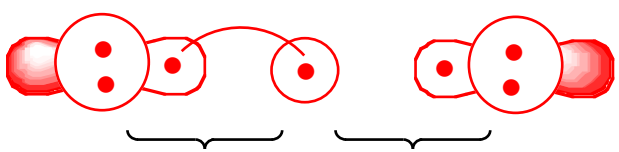

H…F•–•H + mirror image




$\Delta E^{\neq}$ = 62.6 kcal/mol



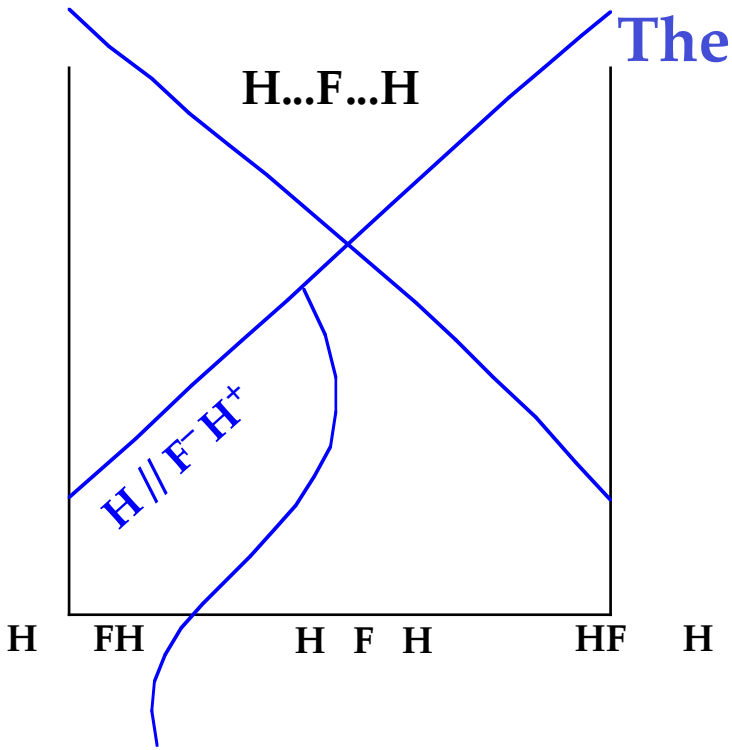

F…H•–•F + mirror image



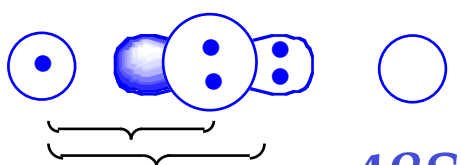

$\Delta E^{\neq}$ = 60.7 kcal/mol

# Illustrations

## The ionic curves



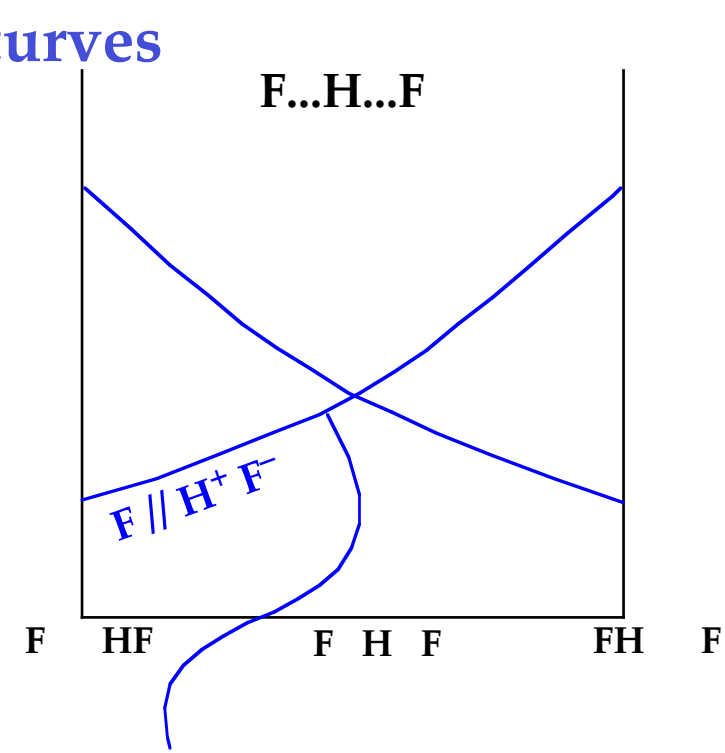

H↑.. F⁻..H⁺ + mirror image



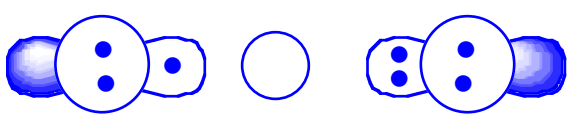
3-e repulsion × 2

–4βS

The ionic structure is strongly destabilized in the transition state




F↑.. H⁺..F⁻ + mirror image



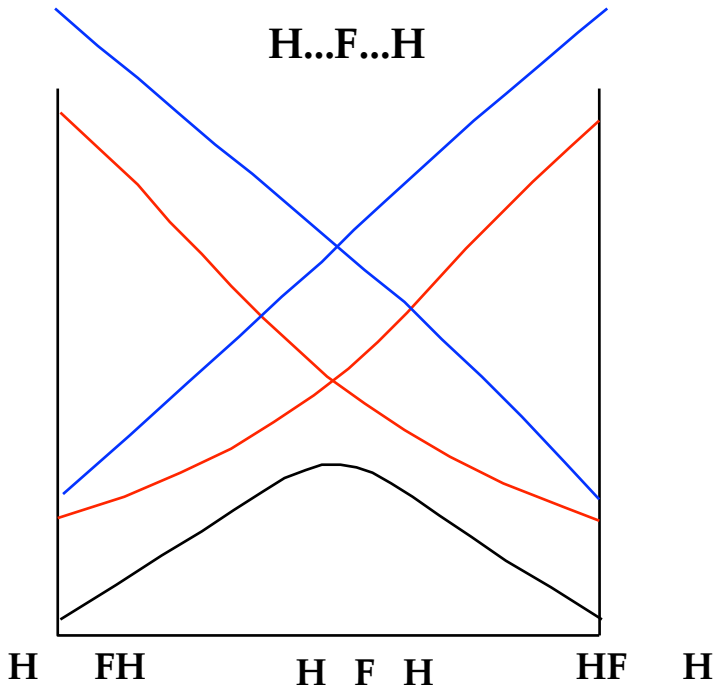
**no** repulsion

0

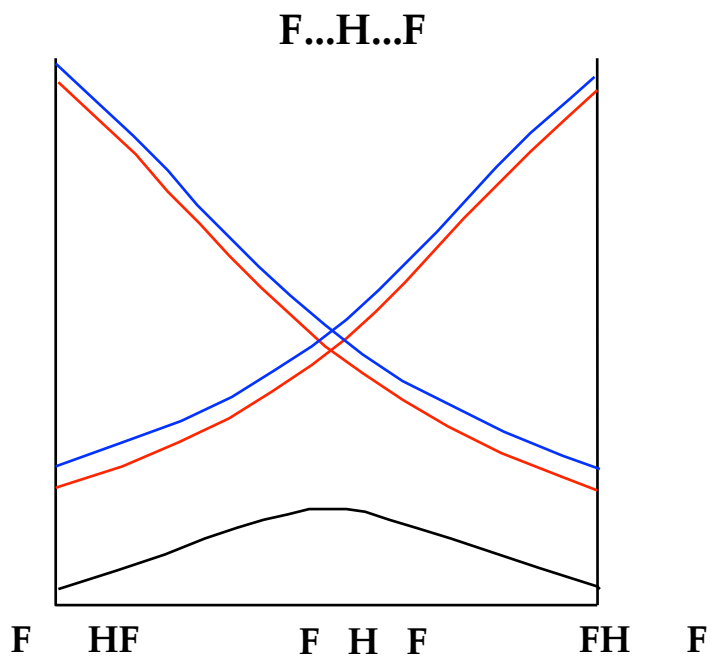
The ionic structure is not destabilized

# Illustrations

**Covalent + ionic curves**




Loss of covalent-ionic RE at the transition state **=> high barrier**

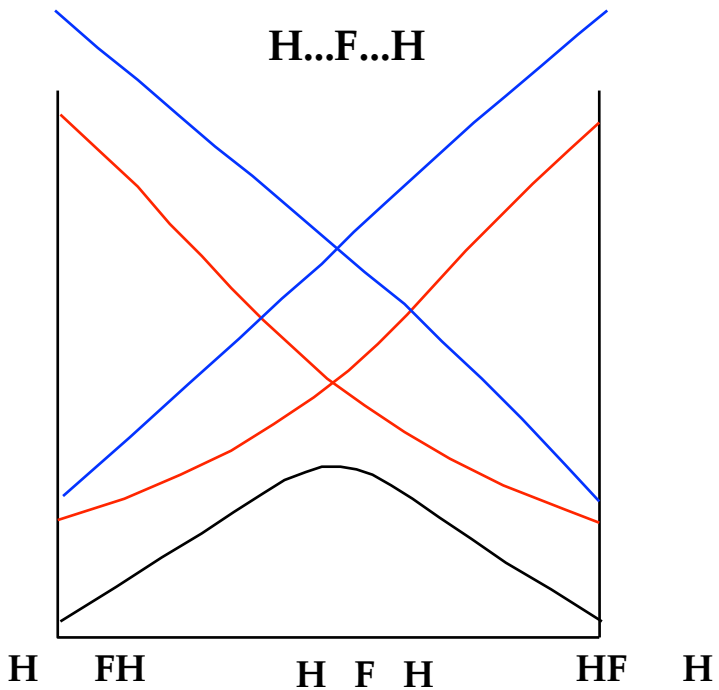



Constant covalent-ionic RE:
**=> lower barrier**

**The only factor that differentiate barriers at the TS is the covalent-ionic RE**

# Illustrations

**Covalent + ionic curves**

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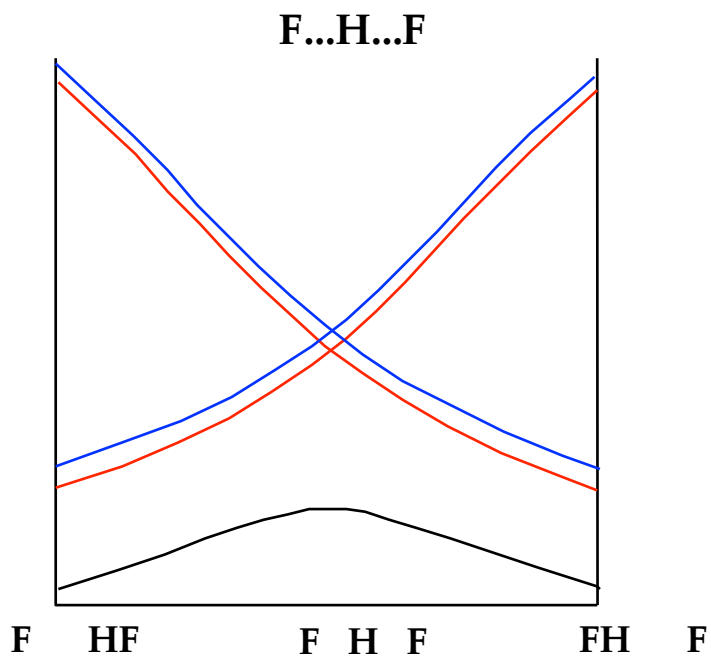
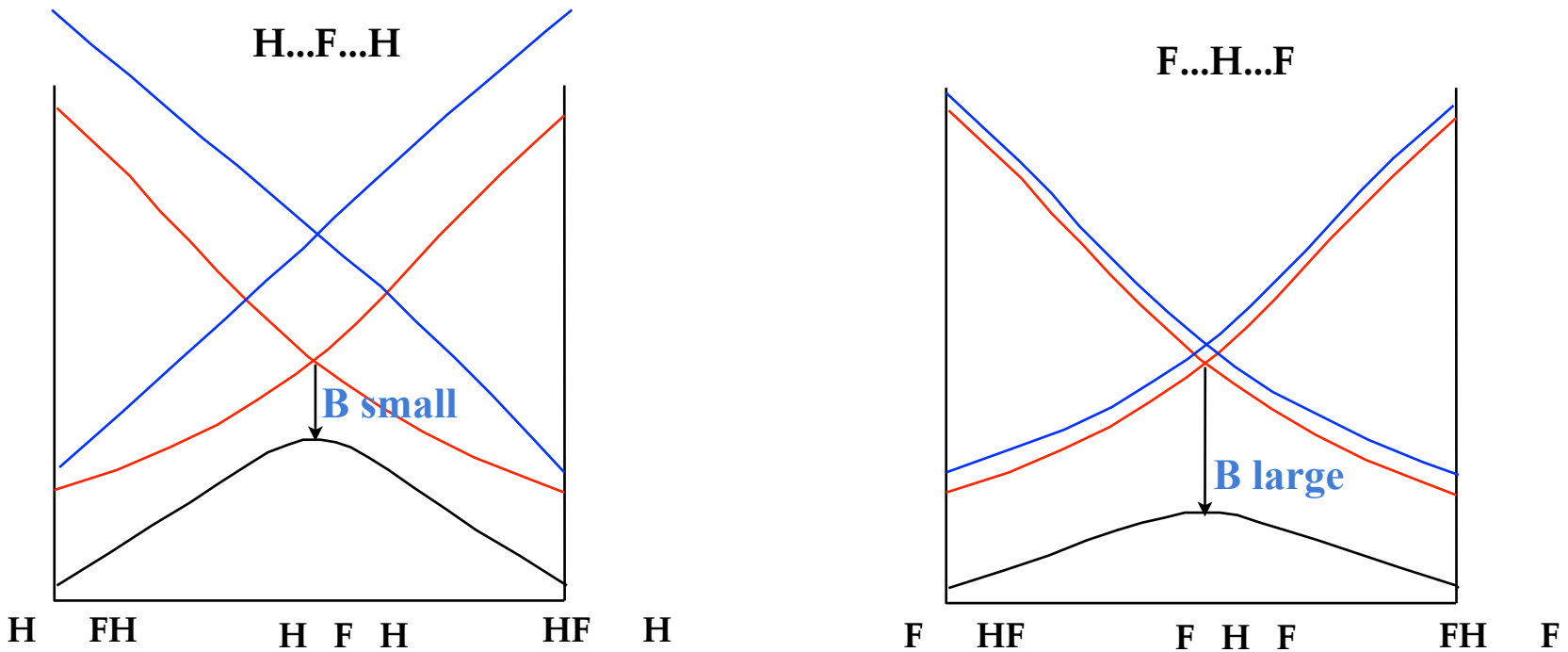



Constant covalent-ionic RE:
**=> lower barrier**

**...and we know (from tutorial 1) that the covalent-ionic RE is very large in H—F**

# Illustrations

**Covalent + ionic curves**




**H…F…H vs. F…H…F**

Resonance Energies (BOVB): **RE(HFH) < RE(FHF)** Difference = **22.3** kcal/mol

Reaction barriers (CCSD(T)): **$\Delta E^{\neq}$(HFH) < $\Delta E^{\neq}$(FHF)** Difference = **21.6** kcal/mol

# Illustrations

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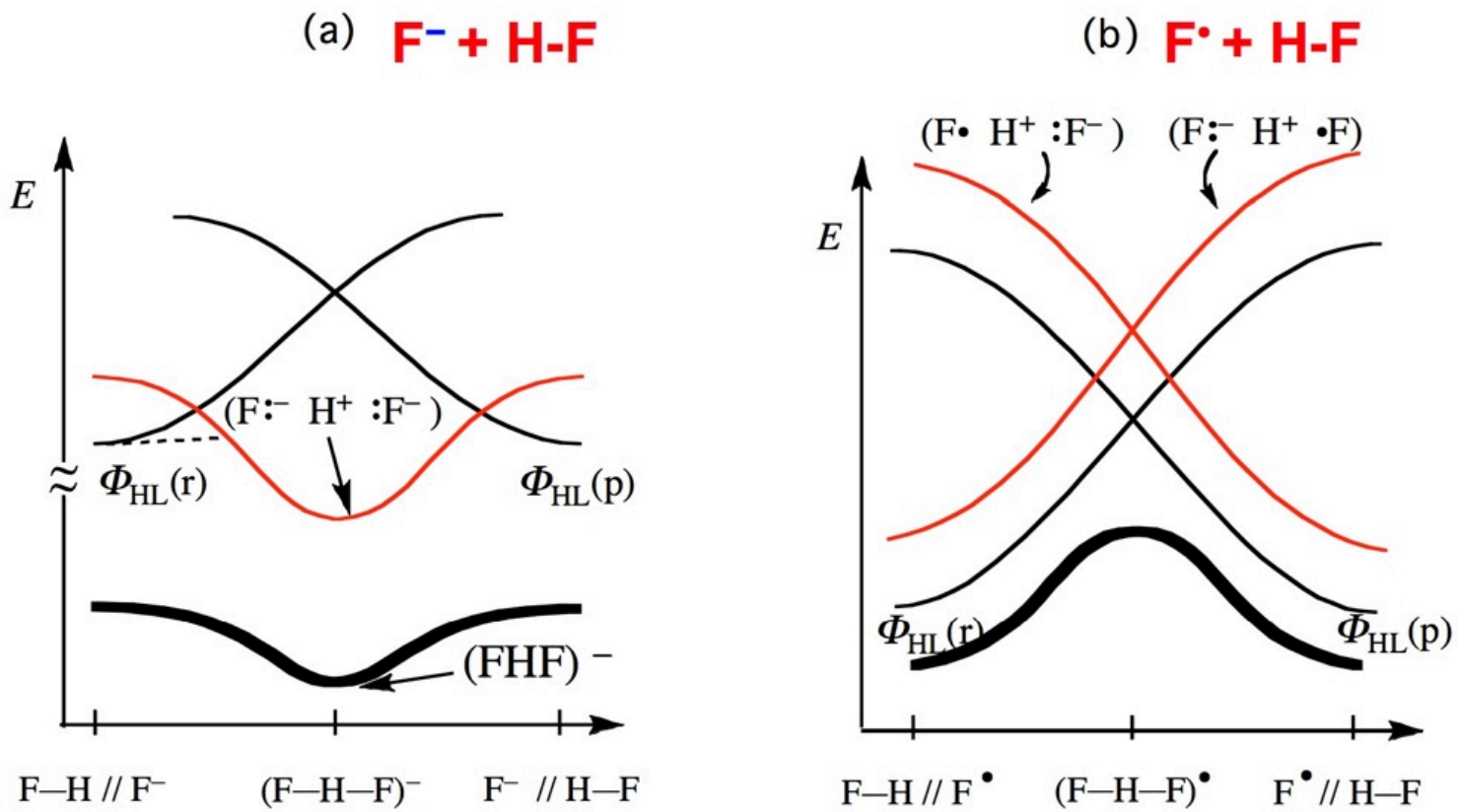
# Illustrations

- Multistate diagrams (VBCMD) :




A single electron may change everything !

# Conclusion

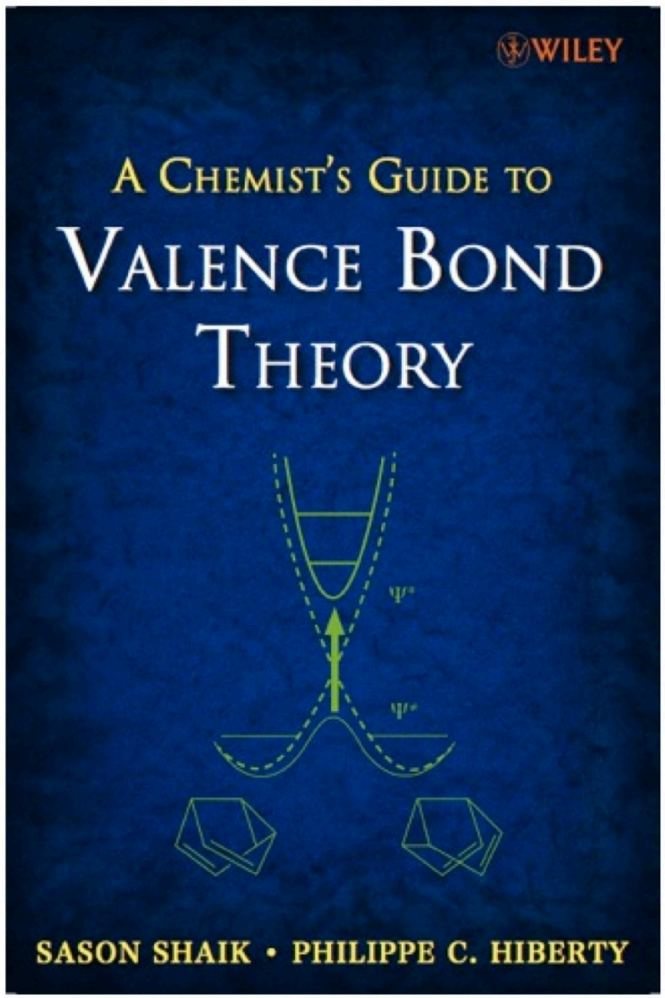
- A general and powerful model for reactivity :
  - Nucleophilic, electrophilic, radical, pericyclic…
  - Simple: could be applied «on the back of en envelop»
  - Insightful: allows to create order among great families of reactions
- Both interpretative and quantitative :
  - qualitative reasonings : a few rules and elementary interactions
  - quantitive proof : by high level VB calculations

# VB theory

➡ VB theory :

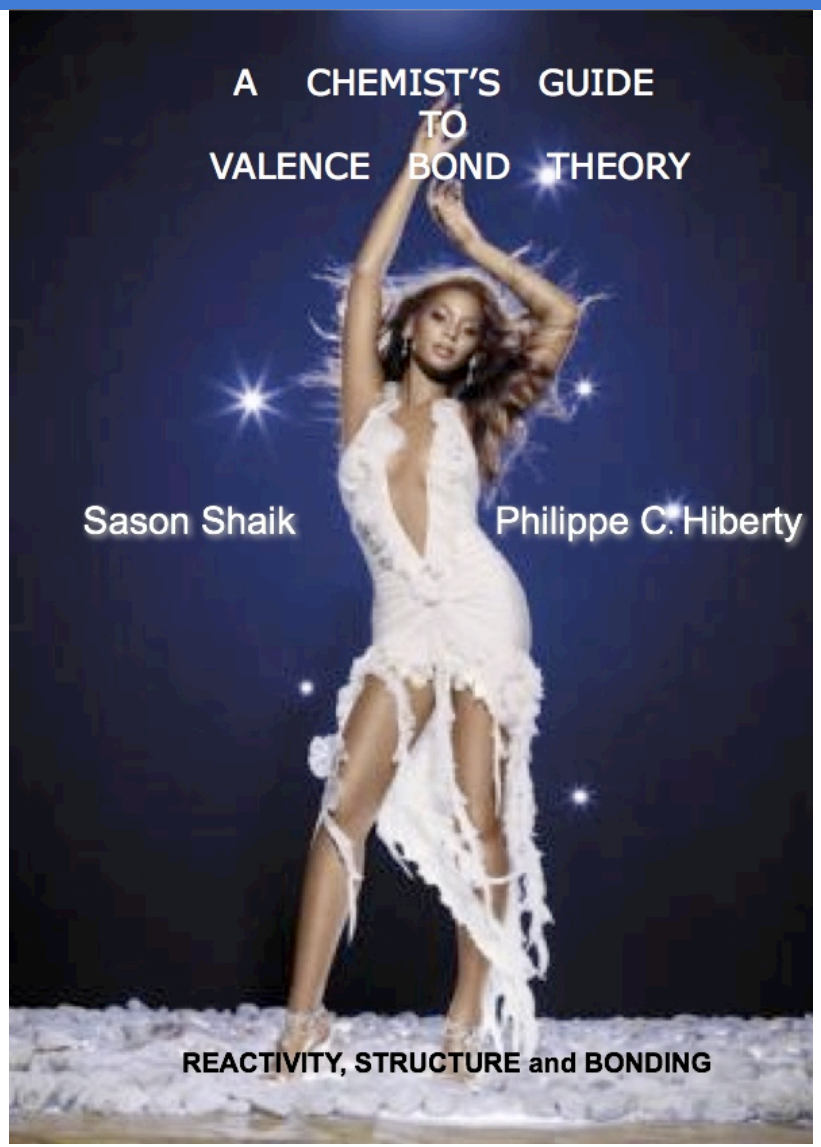
- provides a **wave-function *ansatz*** which enables to compute high level wf that are quantum dressing of Lewis' model ;
- retrieves fundamental **chemical concepts**, such as : resonance / mesomery, hybridization, arrow-pushing language, and provides a theoretical support for them ;
- incorporates **interpretative tools** which are both directly connected to quantum mechanics and to the local vision of chemists' (VB weights, resonance energies, VB diagrams)

# To go further...

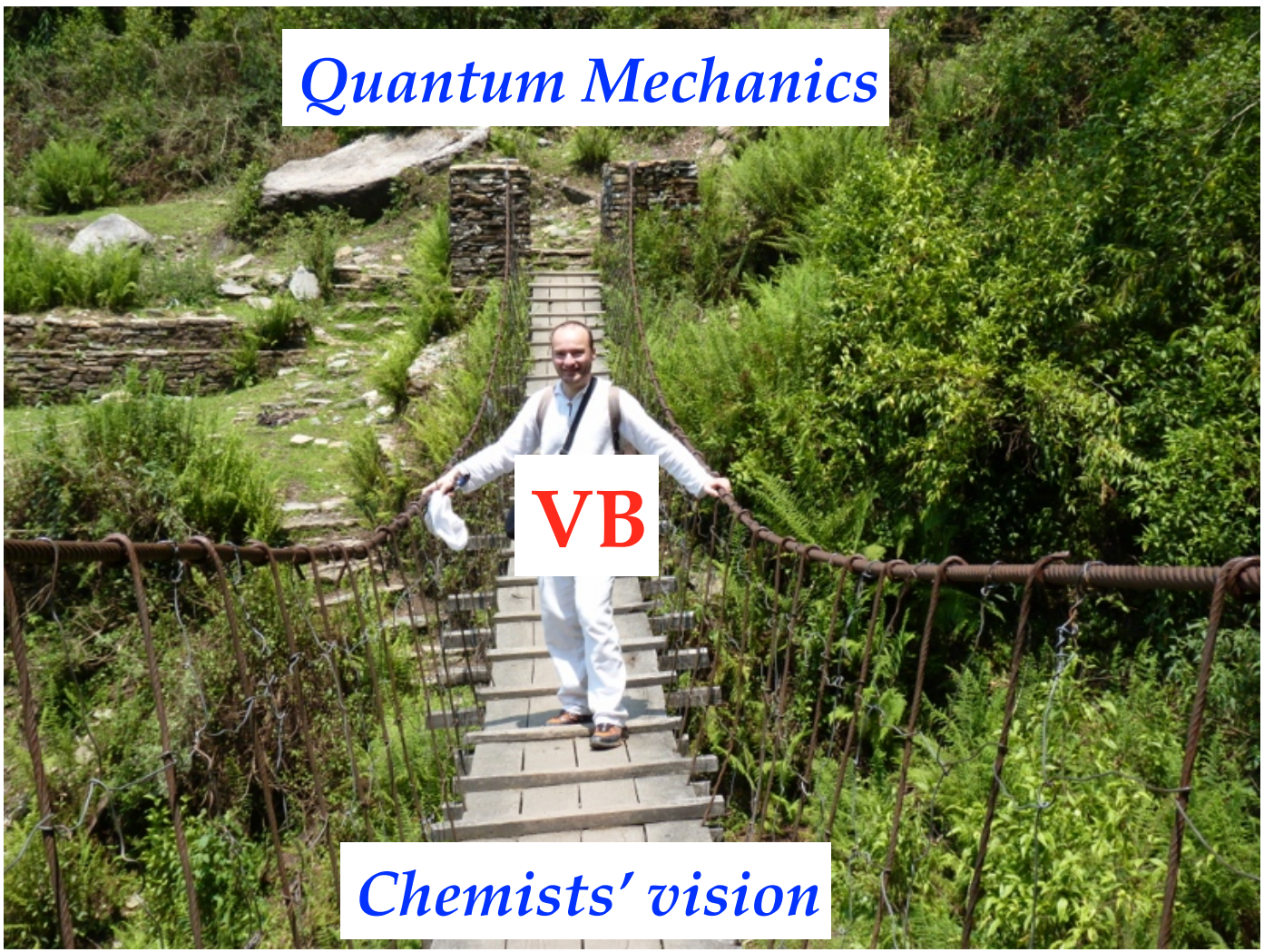



https://wiki.lct.jussieu.fr/workshop/index.php/VB_tutorial

# To go further...



# Final conclusion

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