BONDING AND ADSORPTION:

THEORETICAL ASPECTS

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CONTENT, LITERATURE

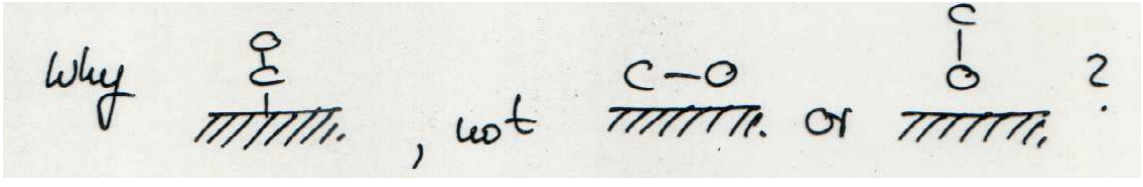
- **Content**

- **Literature**

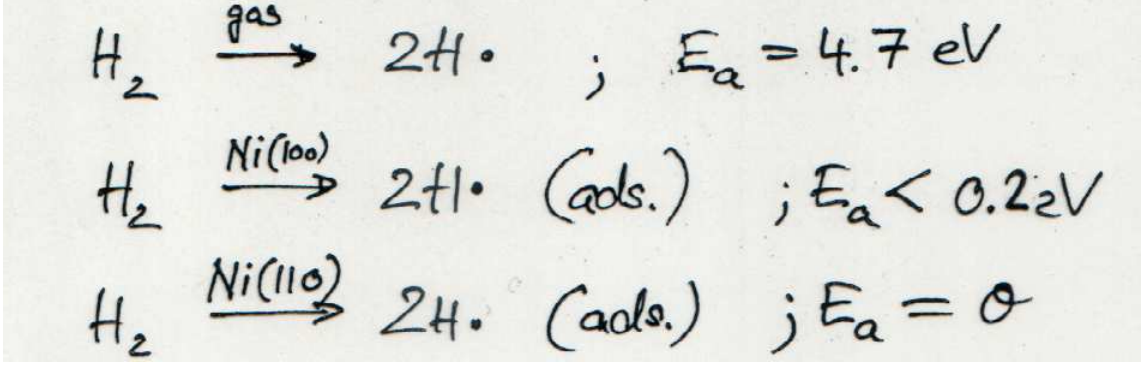
1. A. Groß, "Theoretical Surface Science", Springer Verlag
2. S. Holloway and J. Nørskov, "Bonding at Surfaces", Liverpool University Press
3. R. Hoffmann, "Solids and Surfaces", Wiley

1. Introduction

- **Goals of this lecture**
  - ❶ Understanding why atoms / molecules bind to surfaces
  - ❷ Understanding how they bind to surfaces, e.g.



  - ❸ Understanding what makes a surface reactive, e.g.

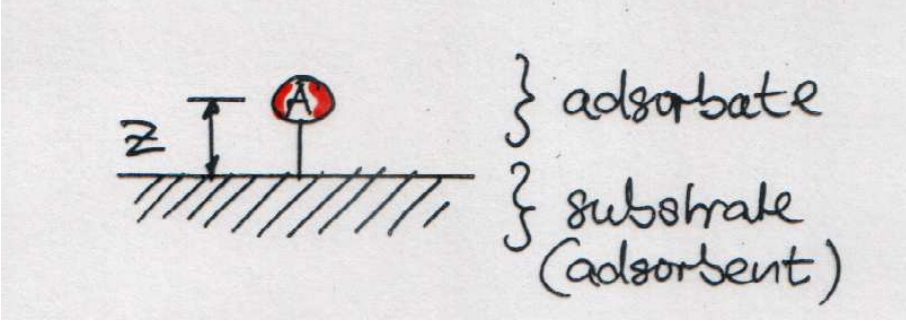


Insight rather than quantitative computation

1. Introduction (cont'd)

- **A few definitions**

  Adsorbent and adsorbate



Adsorption energy E_{ads} and free energy ΔG_{ads}

$$E_{ads} = E_{\text{ads. mol.}} - (E_{\text{free mol.}} + E_{\text{free sub.}}) \sim \Delta U_{ads} \sim \Delta H_{ads}$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$

ΔS_{ads} = entropy change = $S_{\text{ads. mol.}} - S_{\text{free}} < 0$ mostly

$\Longrightarrow$ ΔG_{ads} is usually less negative than $E_{ads} = \Delta U_{ads}$

Here: Adsorption on metal surfaces mostly

2. Physisorption

2.1 Basic characteristics

physisorption = "physical adsorption"

adsorption energy, $\lvert E_{ads}\rvert$	"weak" : $\lesssim$ 0.1 eV–0.2eV
ads.–substr. bond l. z_{ads}	"long" : $\gtrsim$ 2.5 Å
specifity	unspecific
binding mechanism	Van der Waals
Examples	He/Cu, Ne/Cu, H_2/Cu (?)

Role of adsorbate

Role of surface

(He on jellium, DFT)

Role of site

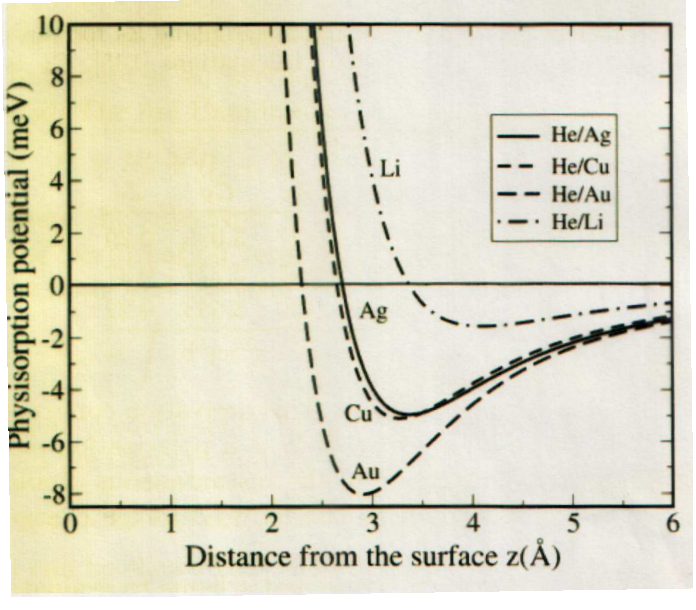
He/Cu*: $E_{ads} \approx$ 6 meV

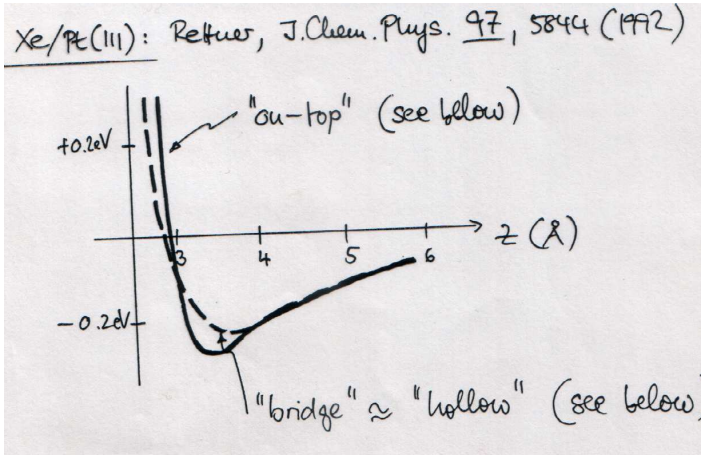
Ne/Cu(100): $E_{ads} \approx$ 12 meV

Ar/Cu(110): $E_{ads} \approx$ 60 meV

H_2/Cu*: $E_{ads} \approx$ 22 meV

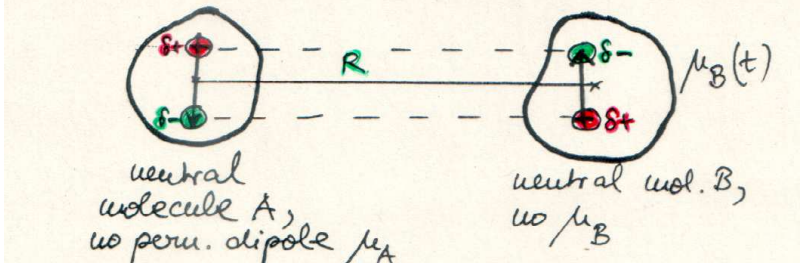
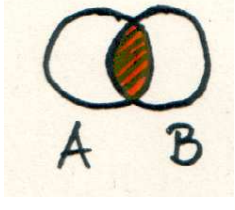
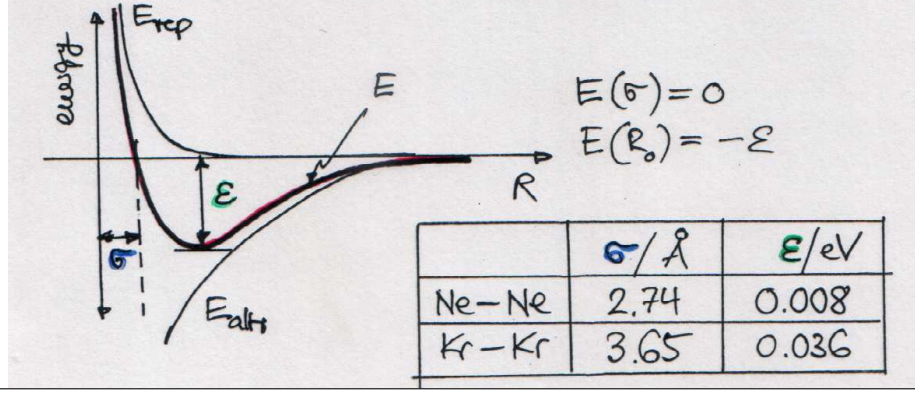
* theory: Phys. Rev. B37, 7306 (1988)





2. Physisorption (cont'd)

2.2 Van der Waals interaction

attractive	repulsive	total
dispersion	Pauli repulsion	Van der Waals interaction
$E_{attr} = -\frac{C}{R^6}$	$E_{rep} = \frac{A}{R^{12}}$	$\boxed{E = \frac{A}{R^{12}} - \frac{C}{R^6}}$
$C = \frac{3}{2}\alpha_A\alpha_B\frac{IP_A IP_B}{IP_A + IP_B}$		or: $\boxed{E = 4\varepsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right\}}$ "12-6 potential"
		

	σ/Å	ε/eV
Ne–Ne	2.74	0.008
Kr–Kr	3.65	0.036

2. Physisorption (cont'd)

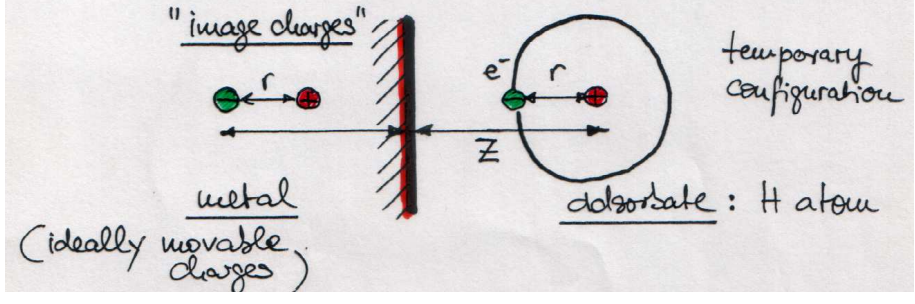
2.3 Van der Waals interactions at metal surfaces

By "infinite sum" over surface-atom interactions, one gets

$$E = \frac{A'}{Z^9} - \frac{C'}{Z^3}$$

"9-3 potential"

Oversimplified model calculation for the attractive part (H atom as an example)



$$E_{attr} = e^2\left[-\frac{1}{2Z} - \frac{1}{2(Z-r)} + 2\frac{1}{2Z-r}\right]$$

$$= e^2\left[\frac{-2(Z-r)(2Z-r) - 2Z(2Z-r) + 8Z(Z-r)}{4Z(Z-r)(2Z-r)}\right] = -\frac{e^2}{2}\left[\frac{r^2}{Z(Z-r)(2Z-r)}\right]$$

In the limit $Z \gg r$ (far from surface): $\boxed{\lim_{Z\gg r} E_{attr} = -\frac{e^2}{4}\frac{r^2}{Z^3}}$

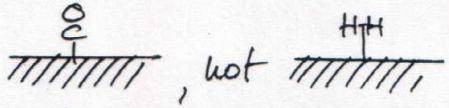
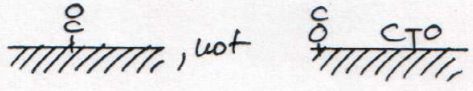
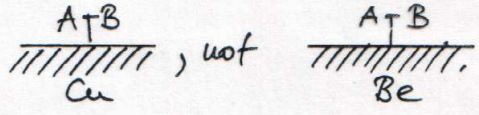
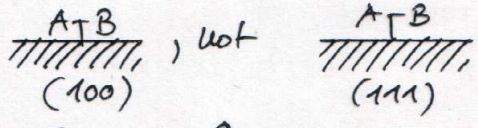
3. Chemisorption

3.1 Basic characteristics

chemisorption = "chemical adsorption"

adsorption energy, $\lvert E_{ads} \rvert$	"large" : $\gtrsim 0.2$ eV
ads.-substr. bond l., Z_{ads}	"short" : $\lesssim 3$ Å
specifity *	highly specific
binding mechanism	"chemical": e.g., covalent
Examples	CO/Cu ; H/Ni ; N/Fe

Specifity*:

specifity	example
molecule : type	
molecule : orientation	
surface : type	
surface : index	
surface : site	

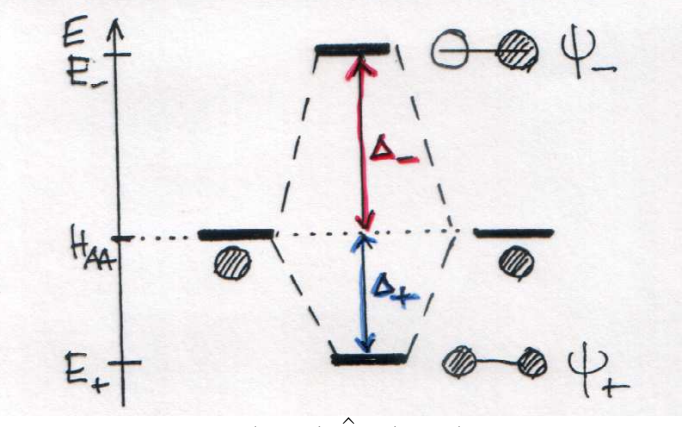
3.2 Chemical bonding in molecules

(1) LCAO-MO theory: The symmetric 2-orbital problem

- Solve *electronic Schrödinger equation* $\boxed{\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}}$ within LCAO-MO
- For 2 atoms, 1 orbital φ (AO) each (e.g. H(1s)), *ansatz* for wavefunction (MO)

$$\boxed{\psi_{el} = C_A\varphi_A + C_B\varphi_B} \qquad C_A, C_B = \text{coefficients}$$

- In the *symmetric orbital case* (e.g., H_2), the SE has two solutions



MO	energy
bonding, $\psi_+ = \frac{1}{\sqrt{2(1+S)}}(\varphi_A+\varphi_B)$	$E_+ = \frac{H_{AA}+H_{AB}}{1+S}$
antibonding, $\psi_- = \frac{1}{\sqrt{2(1-S)}}(\varphi_A-\varphi_B)$	$E_- = \frac{H_{AA}-H_{AB}}{1-S}$

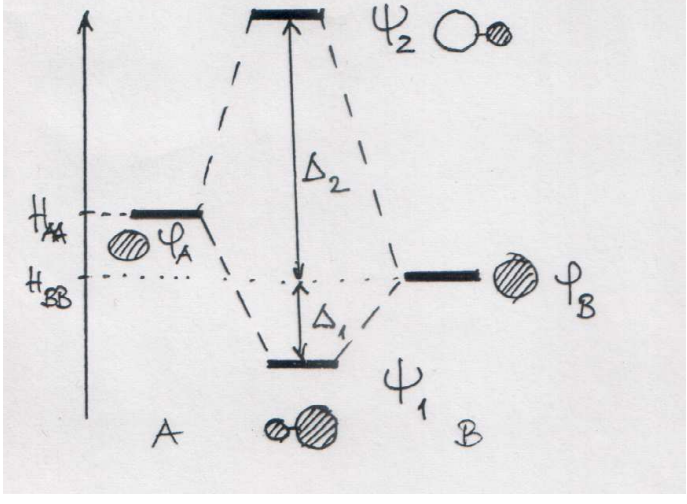
with $H_{AA} = \langle\varphi_A|\hat{H}_{el}|\varphi_A\rangle = H_{BB}$, $H_{AB} = \langle\varphi_A|\hat{H}_{el}|\varphi_B\rangle$, $S = \langle\varphi_A|\varphi_B\rangle$ (overlap integral)

- **Discussion:**
  1. $\Delta_-/\Delta_+ = (1+S)/(1-S) > 1$
  2. occupation $n = 0$: no effect
     occupation $n = 1, 2$: stabilizing
     occupation $n = 4$: destabilizing

3.2 Chemical bonding in molecules (cont'd)

(2) LCAO-MO theory: The asymmetric 2-orbital problem

- For *asymmetric orbital case* ($A \neq B$, 1 orbital each, e.g. H-He):

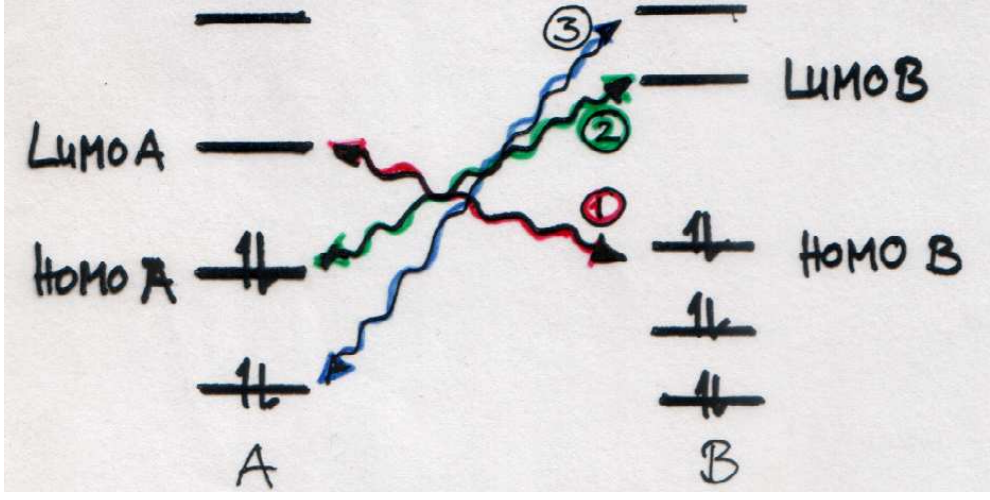


- **Discussion:**
  - ❶ occupation $n = 1, 2$: stabilizing
    occupation $n = 4$: destabilizing
  - ❷ ψ_1 is "B-like", ψ_2 is "A-like" (B=more electronegative)
  - ❸ 2nd order PT: $\boxed{\Delta_1^{(2)} = |H_{AB}|^2/(H_{AA} - H_{BB})}$
    - Δ_1 (mixing) small, if $|H_{AA} - H_{BB}|$ large
    - Δ_1 small, if H_{AB} small or zero

      note: $H_{AB} \sim KS(H_{AA} + H_{BB})$ (Wolfsberg-Helmholtz)

3.2 Chemical bonding in molecules (cont'd)

(3) LCAO-MO theory: The N-orbital, 2-atom problem



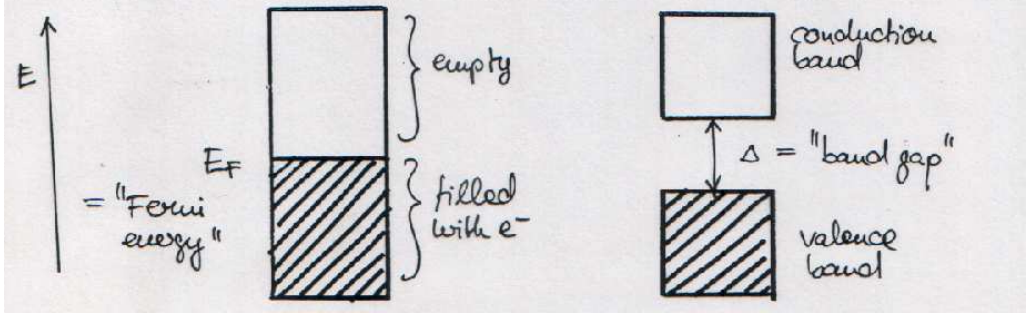
- **Discussion:**
  - ① (LUMO A / HOMO B) > ② (LUMO B / HOMO A) ≫ ③ $(H_{L_AL_A} - H_{H_BH_B}) < (H_{L_BL_B} - H_{H_AH_A}) < (H_{i_Bi_B} - H_{j_Aj_A})$
  - Interactions between close-lying empty orbitals (n=0) or full orbitals (n=4) have no effect or are non-bonding
  - HOMO-LUMO interactions control interatomic interactions

frontier orbital perspective

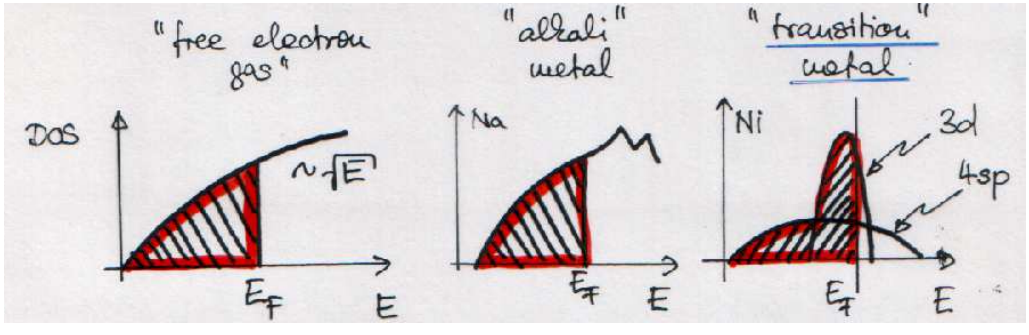
3.3 Chemical bonding at surfaces

(1) A simple model for a metal surface: Bands

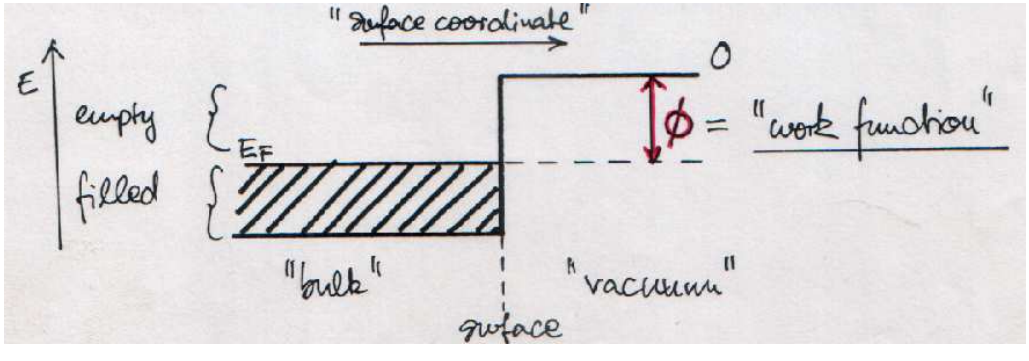
- Energetic picture: Metal vs. semiconductor / insulator



- Density of states (DOS) for metals

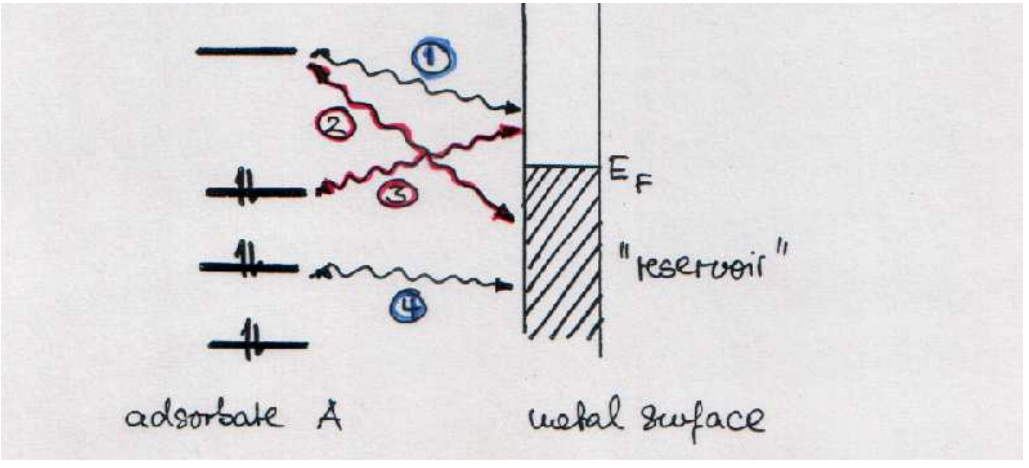


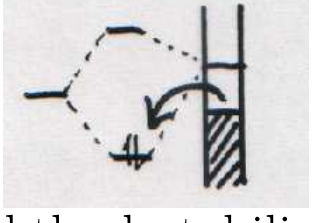
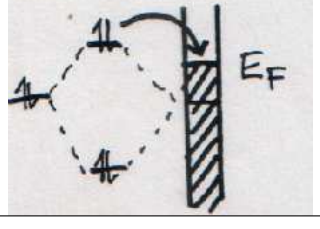
- Surfaces: Energetic / spatial picture



3.3 Chemical bonding at surfaces (cont'd)

(2) Chemical adsorption: Orbital interaction picture

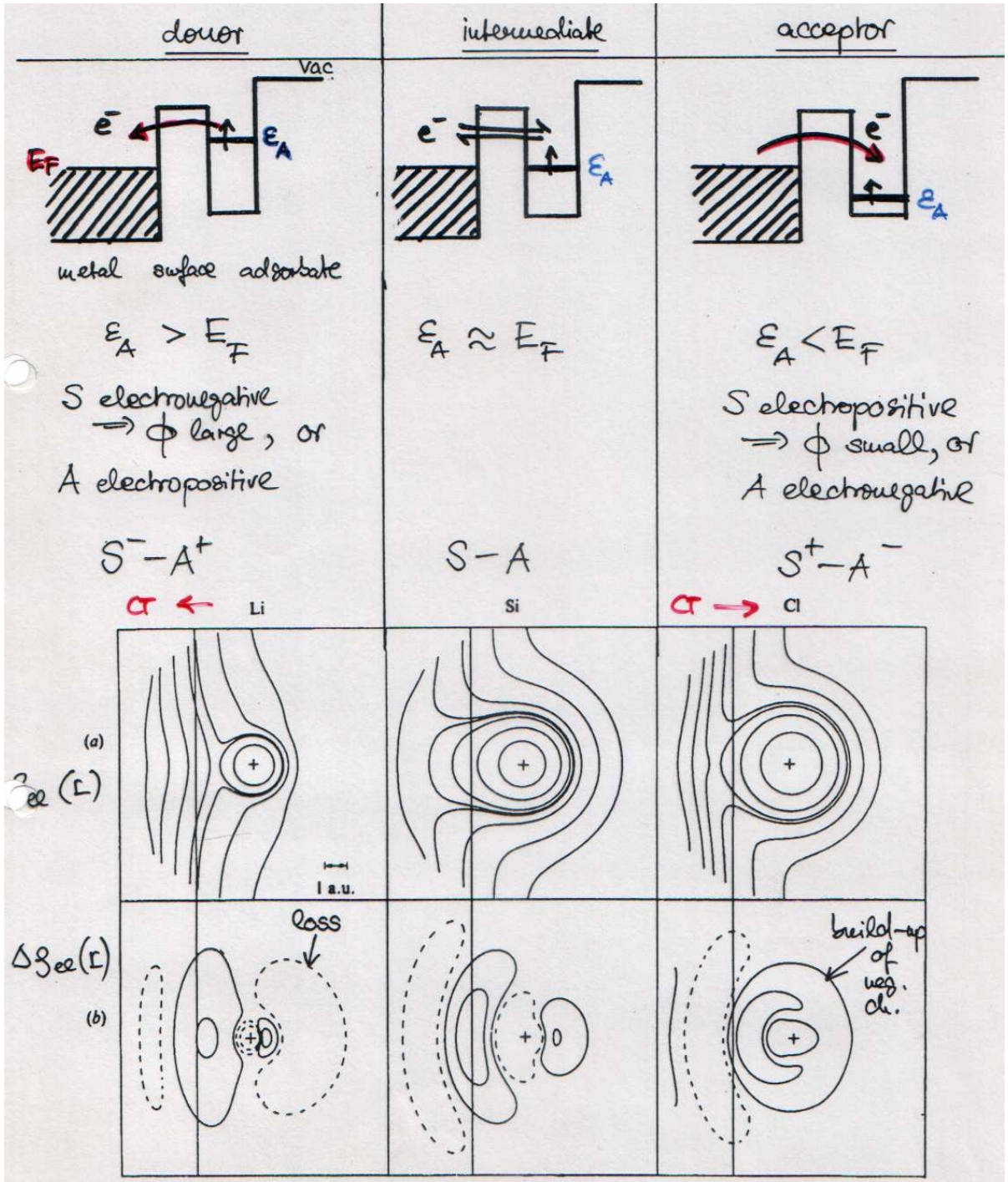


type	energetic effect	other effects
③ 2e-2 "orbital"	stabilizing	A → surface CT; A-S bond formation
② 2e-2 "orbital"	stabilizing	surface → A CT; A-S bond formation
① 0e-2 "orbital"	weakly stabilizing	surface → A CT; A-S bond formation
		
④ 4e-2 "orbital"	slightly destabilizing	A → surface CT; A-S bond formation
		

A-surface bonds tend to form easier than A-B bonds

3.3 Chemical bonding at surfaces (cont'd)

(2) Chemical adsorption:
Energetic / spatial picture
Case 1: Single-level atoms



Adsorption of Li, Si, Cl on "jellium":
Lang, Williams, PRB **18**, 616 (1978)

3.3 Chemical bonding at surfaces (cont'd)

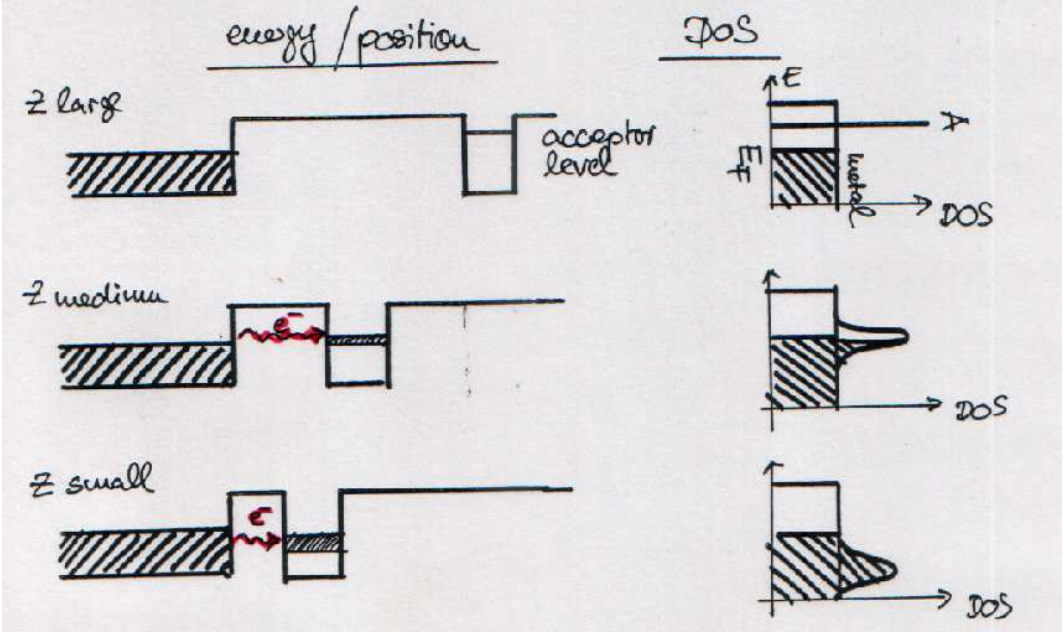
(2) Chemical adsorption: Energetic / spatial picture

Case 1: Single-level atoms, a distance-dependent, closer look

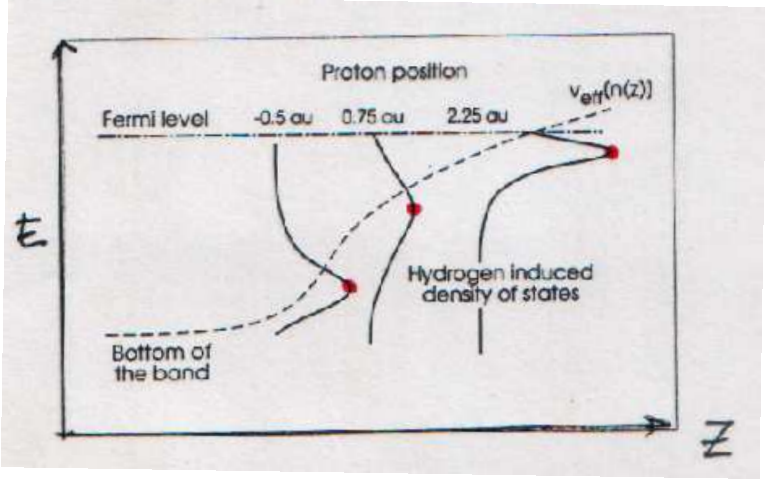
acceptor levels shift and broaden

$$\boxed{\varepsilon_a \sim \varepsilon_a^{\infty} - 1/4Z}$$

$$\boxed{\Delta E \propto e^{-\lambda Z}}$$



Example: H^+ on jellium (PRB **18**, 616 (1978))



(Lorentzian) resonance width: $\boxed{\Delta E = \frac{h}{\tau}}$

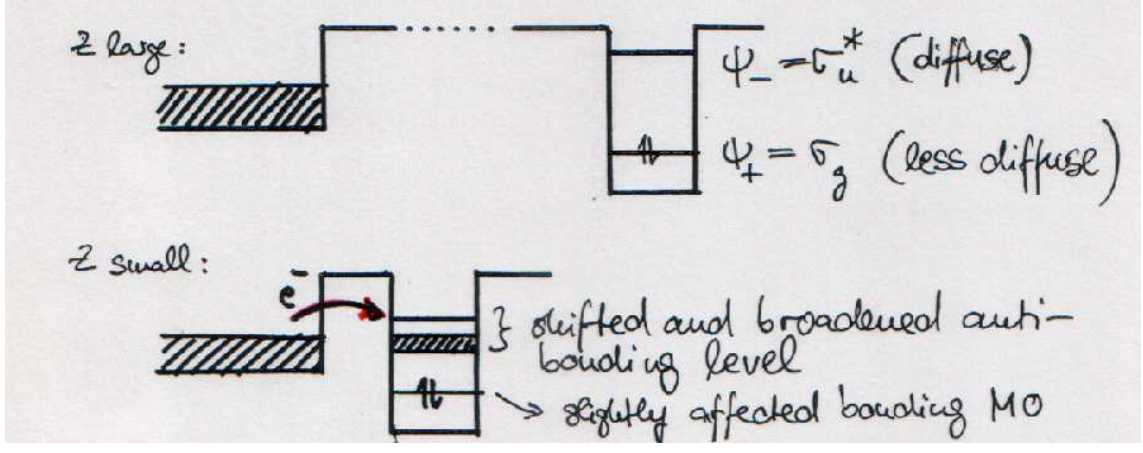
τ =tunneling time

3.3 Chemical bonding at surfaces (cont'd)

(2) Chemical adsorption: Energetic / spatial picture

Case 2: Molecules

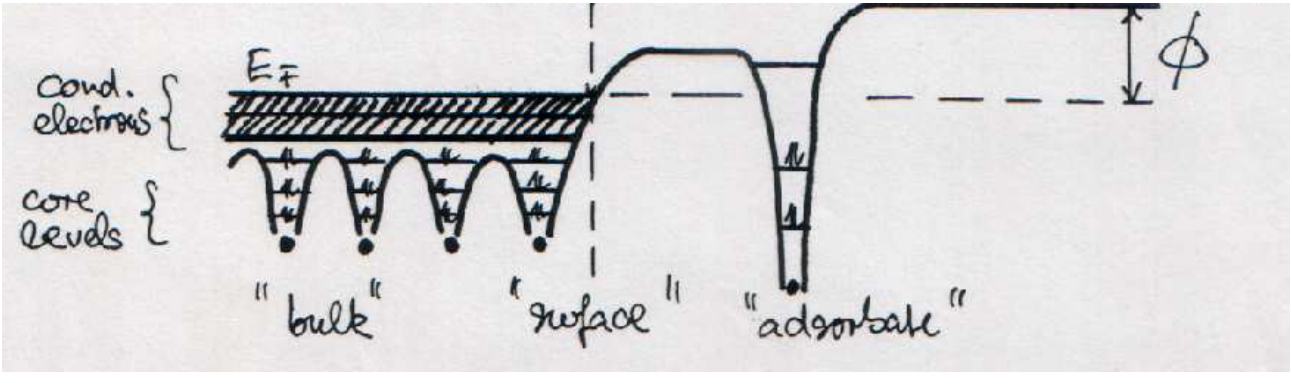
example: H_2 / metal surface



- weakening of H-H (A-B) bond
- strengthening of H-surface bond

LUMO (A) often dominates interaction

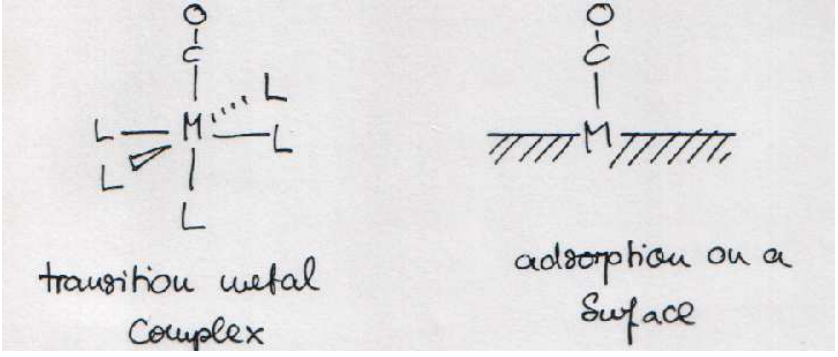
- **A slight refinement of the energetic / spatial picture**



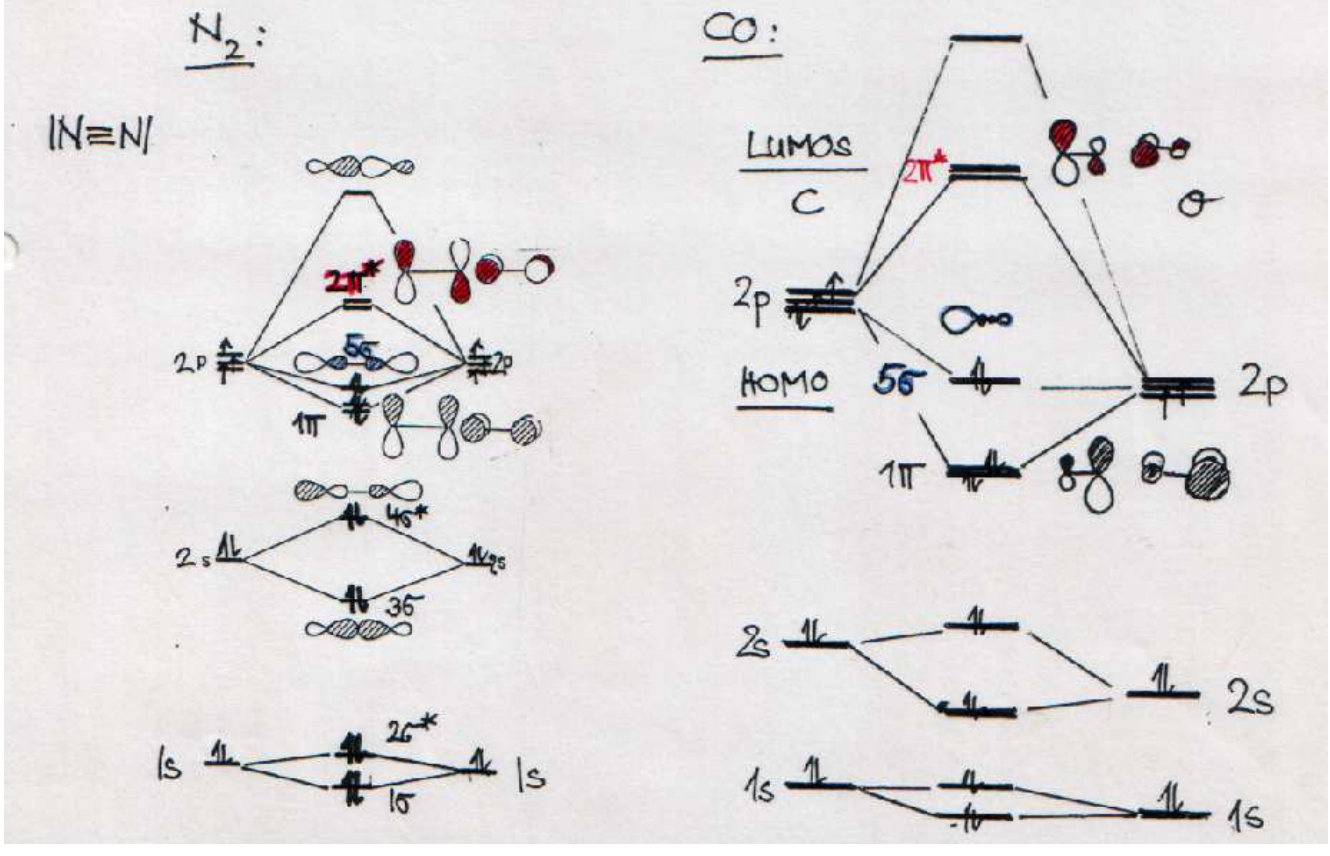
3.4 Chemisorption of CO as a case study

(1) General binding mechanism

a useful analogy:



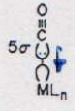
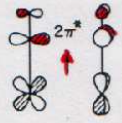
MOs of N_2 and CO:



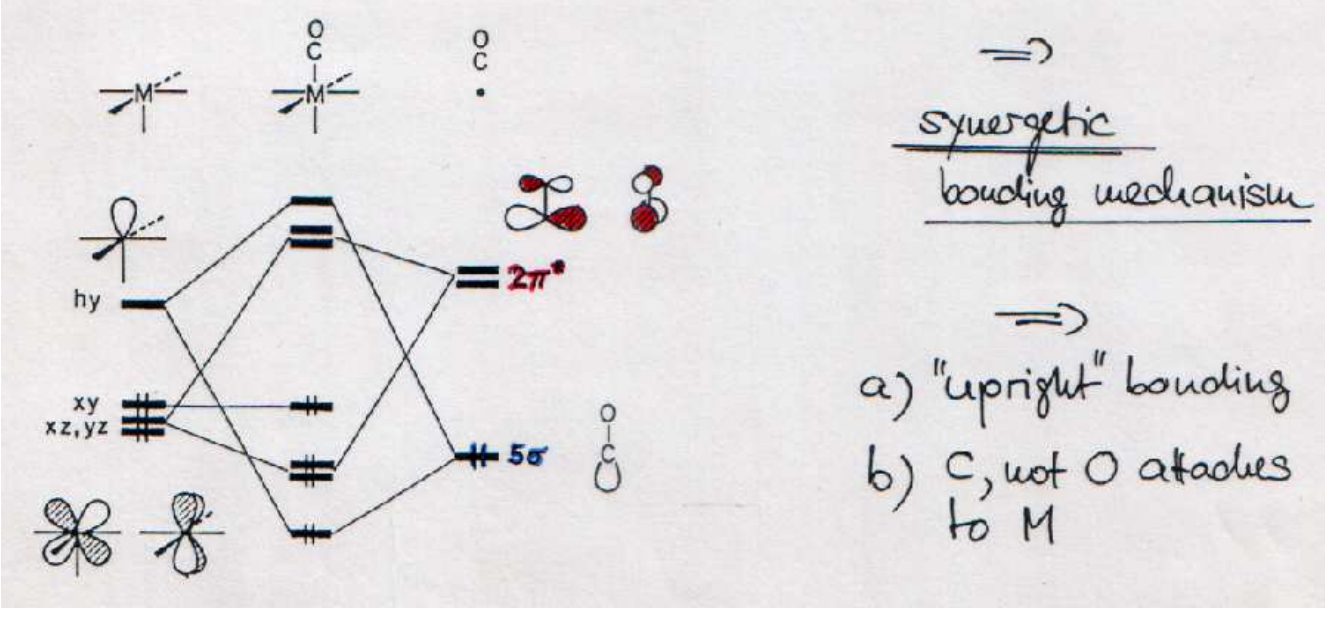
3.4 Chemisorption of CO as a case study

(1) General binding mechanism: CO bonding in TM complexes

dominant interactions:

type	①	②
		
metal orbitals	"d_σ" : d_{z^2}, s, p_z	"d_π" = d_{xz}, d_{yz}
CO orbitals	5σ : donor	2π* : acceptor
action	CO → M CT (weakens CO bond) strengthens M-C bond	M → CO CT weakens CO bond strengthens M-C bond

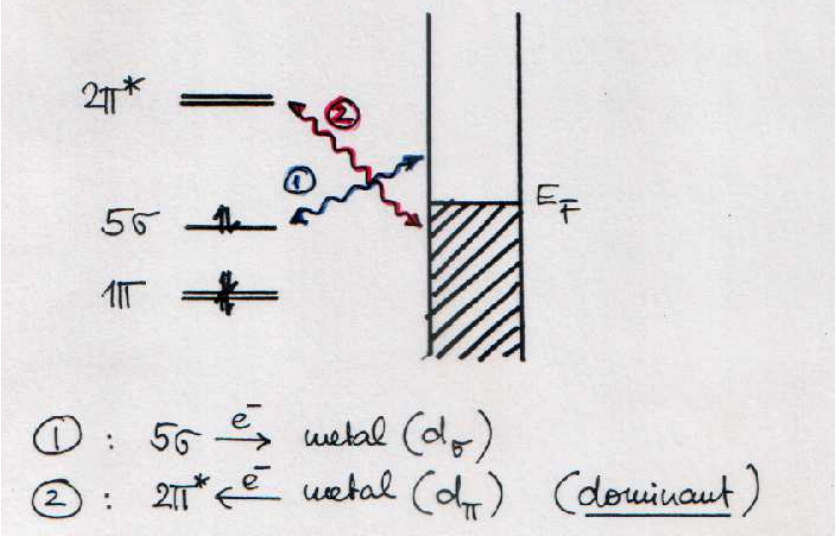
more complete picture:



3.4 Chemisorption of CO as a case study (cont'd)

(1) General binding mechanism: CO bonding to TM surfaces

dominant interactions:



Blyholder model

- **Consequences of synergetic bonding mechanism**

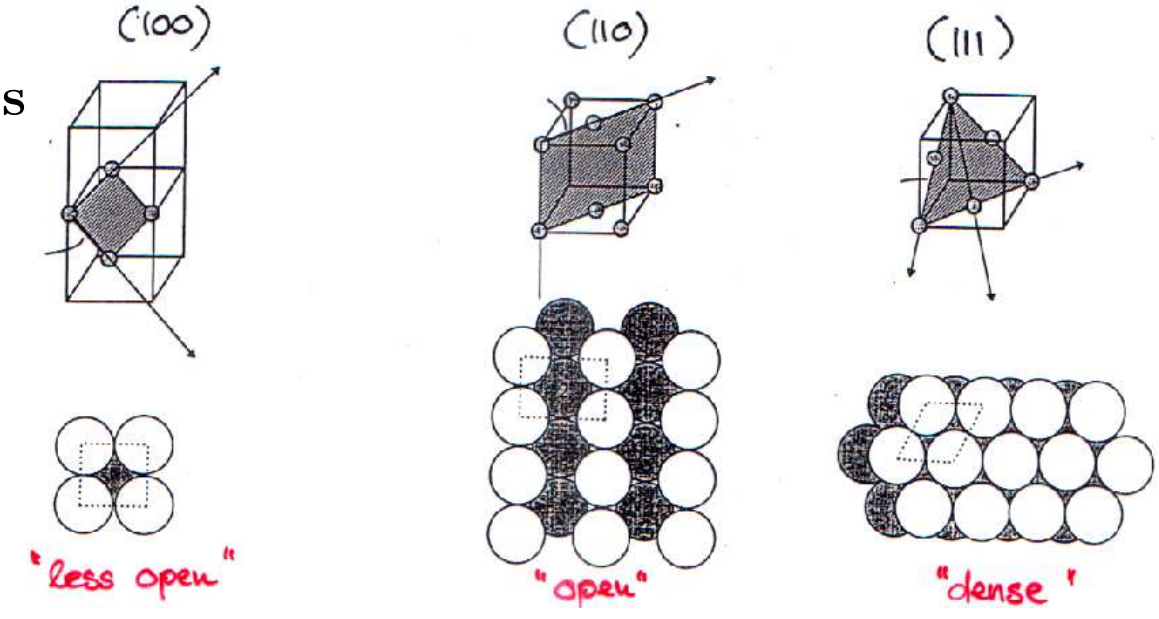
1. C-O bond weakening
   - C-O bond becomes longer
   - C-O stretch frequency $\tilde{\nu}$ becomes smaller
2. M-C bond formation
3. Approximate charge neutrality
4. Consequences
   - linear upright orientation of CO
   - binding via C to M, not O to M

3.4 Chemisorption of CO as a case study (cnt'd)

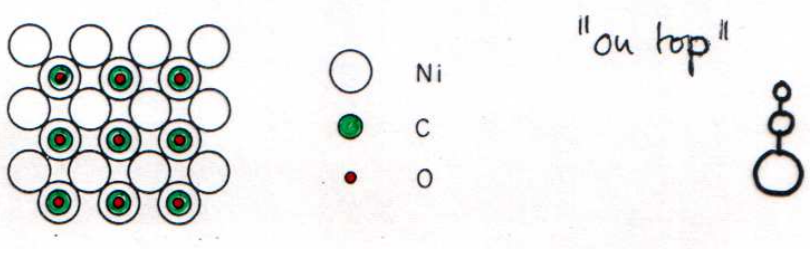
(2) Example: CO on Ni(100)

- **Cuts through metal surfaces**

  (face centered cubic, fcc)



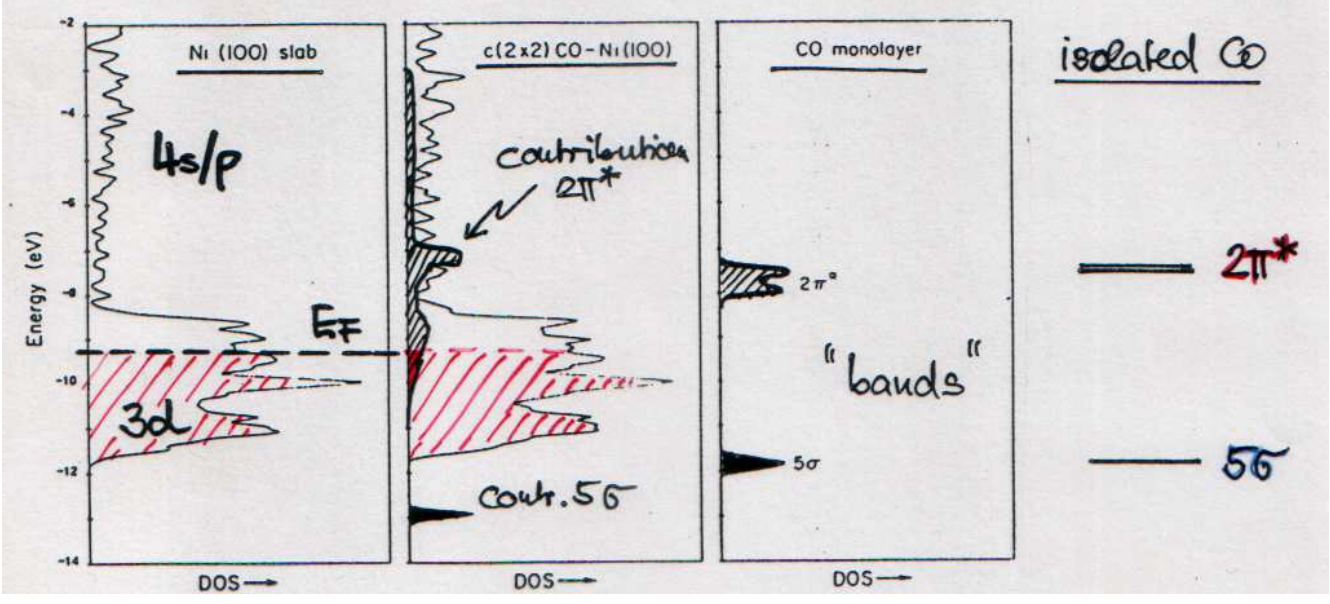
- **c(2×2) CO-Ni(100): (Extended Hückel) Charges**



	free CO + free Ni(100)		c(2x2)CO-Ni(100)	Δ
CO	$n(5\sigma)$	2.0	1.43	−0.38
	$n(2\pi^*)$	0.0	0.74	+0.74
	n_{tot}	14.0	14.25	+0.25
	$\tilde{\nu}$ (exp.)	2143 cm^{-1}	2069 cm^{-1}	−74 cm^{-1}
Ni (which binds to CO)	$n(d_\sigma)$	1.93	1.43	−0.50
	$n(d_\pi)$	3.81	3.31	−0.50
	n_{tot}	28.17	27.37	−0.80

3.4 Chemisorption of CO as a case study (cont'd)

- **c(2×2)CO-Ni(100): Density of states** (EHT calculation)



- **Other adsorption sites: CO/Ni(100)**

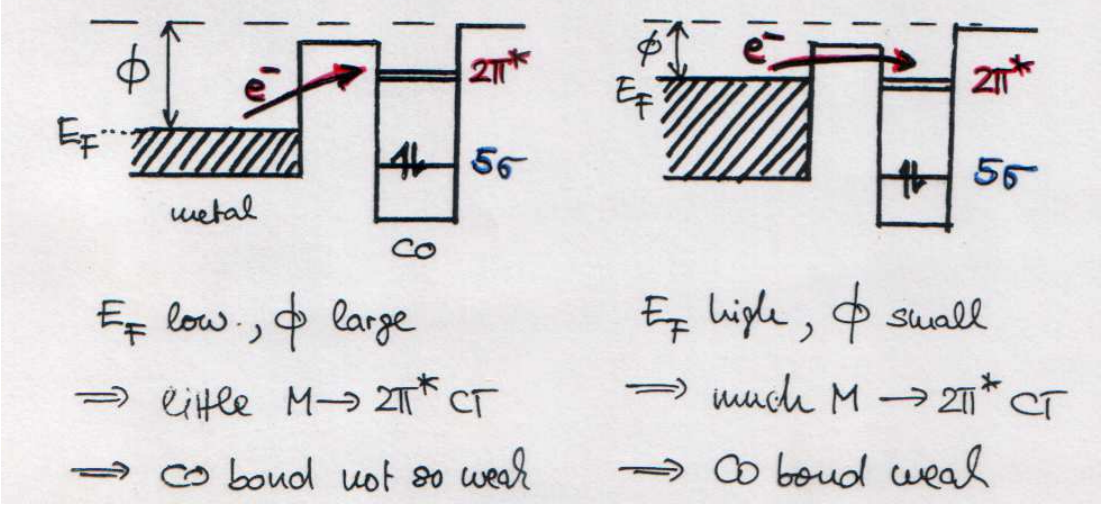
site	on-top	bridge	centre
stability $\tilde{\nu}$ (CO)	most stable 2069 cm^{-1}	metastable 1900 cm^{-1}	metastable 1800 cm^{-1}

- more metal atoms
- stronger back-donation, weaker C-O bond, smaller $\tilde{\nu}$
- analogy metal carbonyls

3.4 Chemisorption of CO as a case study (cont'd)

(3) Trends in CO chemisorption

- **Effect of adsorption site:** Large coordination $\Longrightarrow$ weak C-O bond
- **Effect of crystal face:**
  Effect of workfunction Φ
  (or Fermi energy E_F)



Example: CO on various Ni faces
(EHT results)

	Ni(110)	Ni(100)	Ni(111)
Φ	5.04 eV	5.22 eV	5.35 eV
$\tilde{\nu}$(CO) (a)	1990 cm^{-1}	2069	2045
$\tilde{\nu}$(CO) (b)	1880	1900	1919
$\tilde{\nu}$(CO) (c)	1565	1800	1817

(a) = on top, (b) = bridge, (c) = hollow

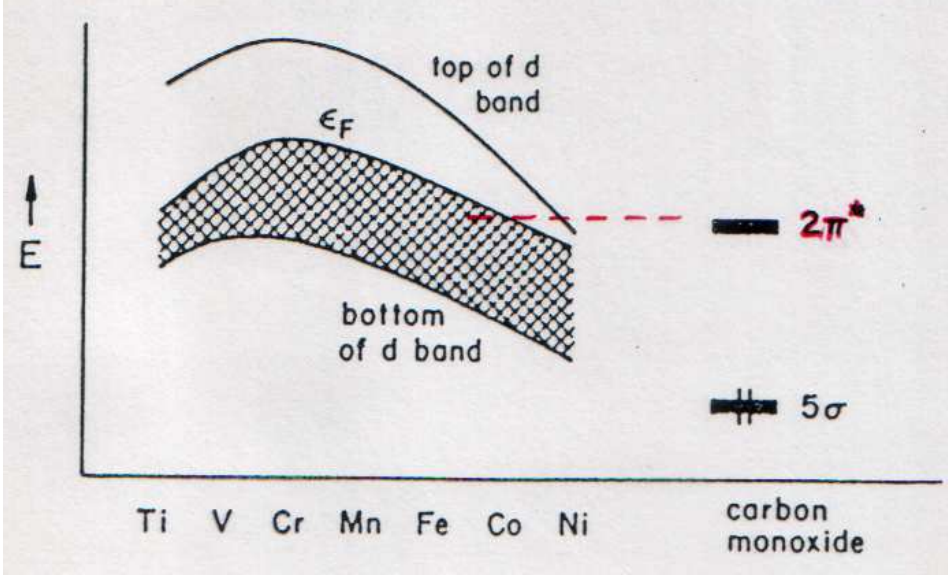
increasing Φ

increasing "openess", reactivity

3.4 Chemisorption of CO as a case study (cont'd)

(3) Trends in CO chemisorption

- **Effect of metal type:**



Trends for transition metals (from Ti $\rightarrow$ Ni):

❶ Increasing $Z \Longrightarrow$
more contracted d-orbitals

❷ Increasing $Z \Longrightarrow$
higher ionization potential (lower E_F, larger Φ)

early TM more reactive

Charges for TM/CO (EHT calculation)

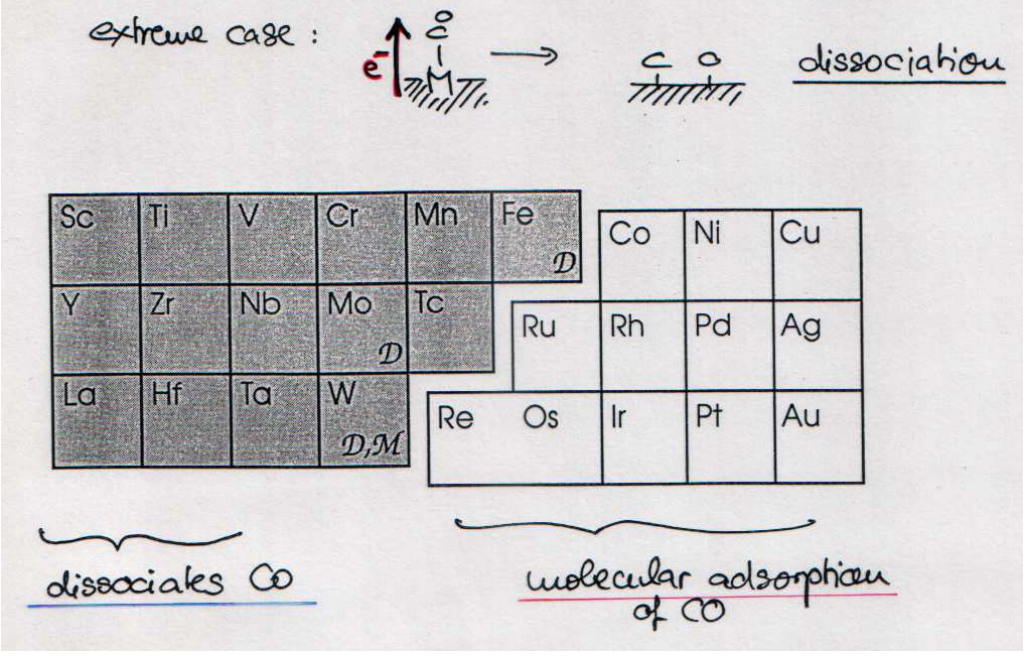
metal	Ti (0001)	Cr (110)	Fe (110)	Co (0001)	Ni (100)	Ni (111)
n (5σ)	1.73	1.67	1.62	1.60	1.60	1.59
n ($2\pi^*$)	1.61	0.74	0.54	0.43	0.39	0.40

stronger M $\rightarrow 2\pi^*$ back donation

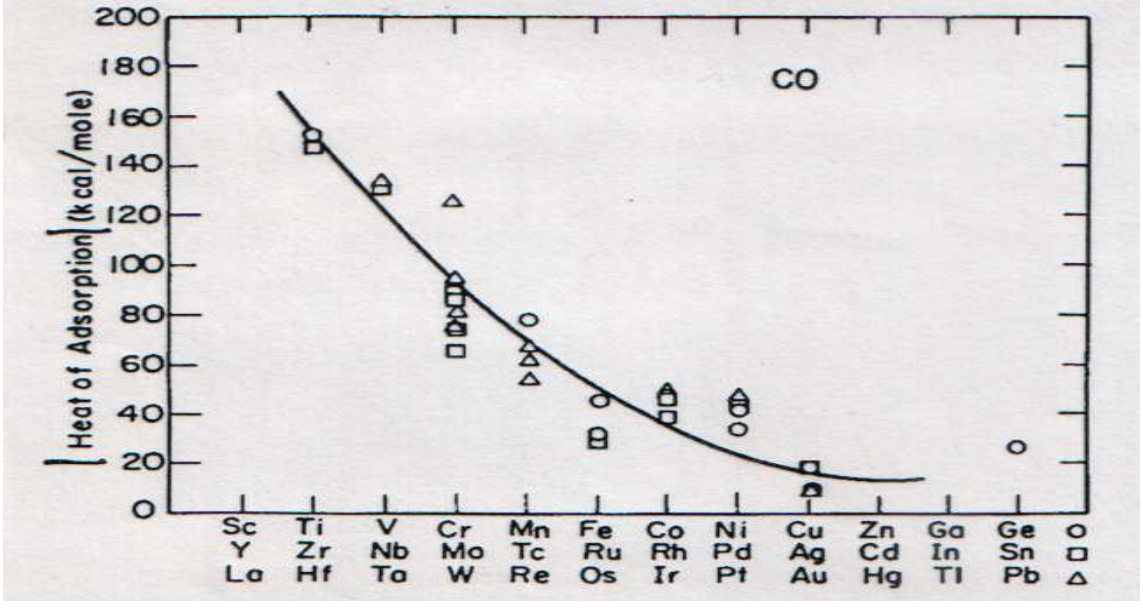
3.4 Chemisorption of CO as a case study (cont'd)

(3) Trends in CO chemisorption

- **Breaking C-O bonds:**



Binding energies



approximate relation:

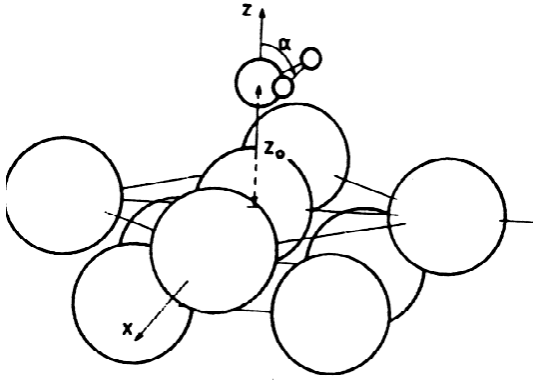
$\Delta H_{ads} \sim \mathrm{M} \rightarrow 2\pi^*$ back-donation

4. Adsorption from "first principles"

4.1 Models

(1) Cluster models

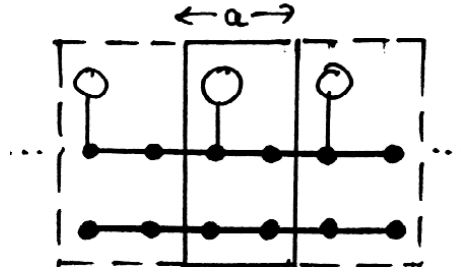
e.g. H_2O/Al_9



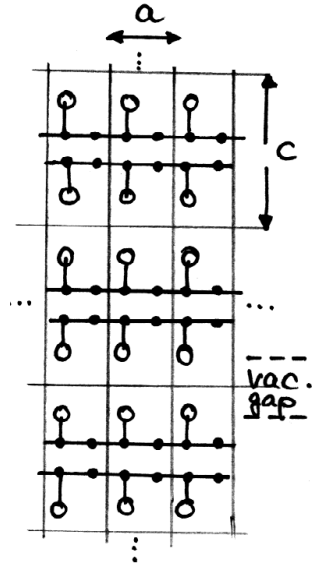
advantages	disadvantages
• molecular $\Longrightarrow$ quantum chemistry • excited states • good for insulators, semiconductors	• boundary effects $\Longrightarrow$ embedding • which cluster? • bad for metals

(2) Periodic models

slab models



supercell models



advantages	disadvantages
• no lateral boundaries • faster convergence • high coverage • metals: $D(E_F)$	• low coverage • impurities • excited states • periodicity along z

Baerends *et al.*, Chem. Phys. **177**, 399 (1993)

4.2 Electronic structure methods

(1) Overview over methods

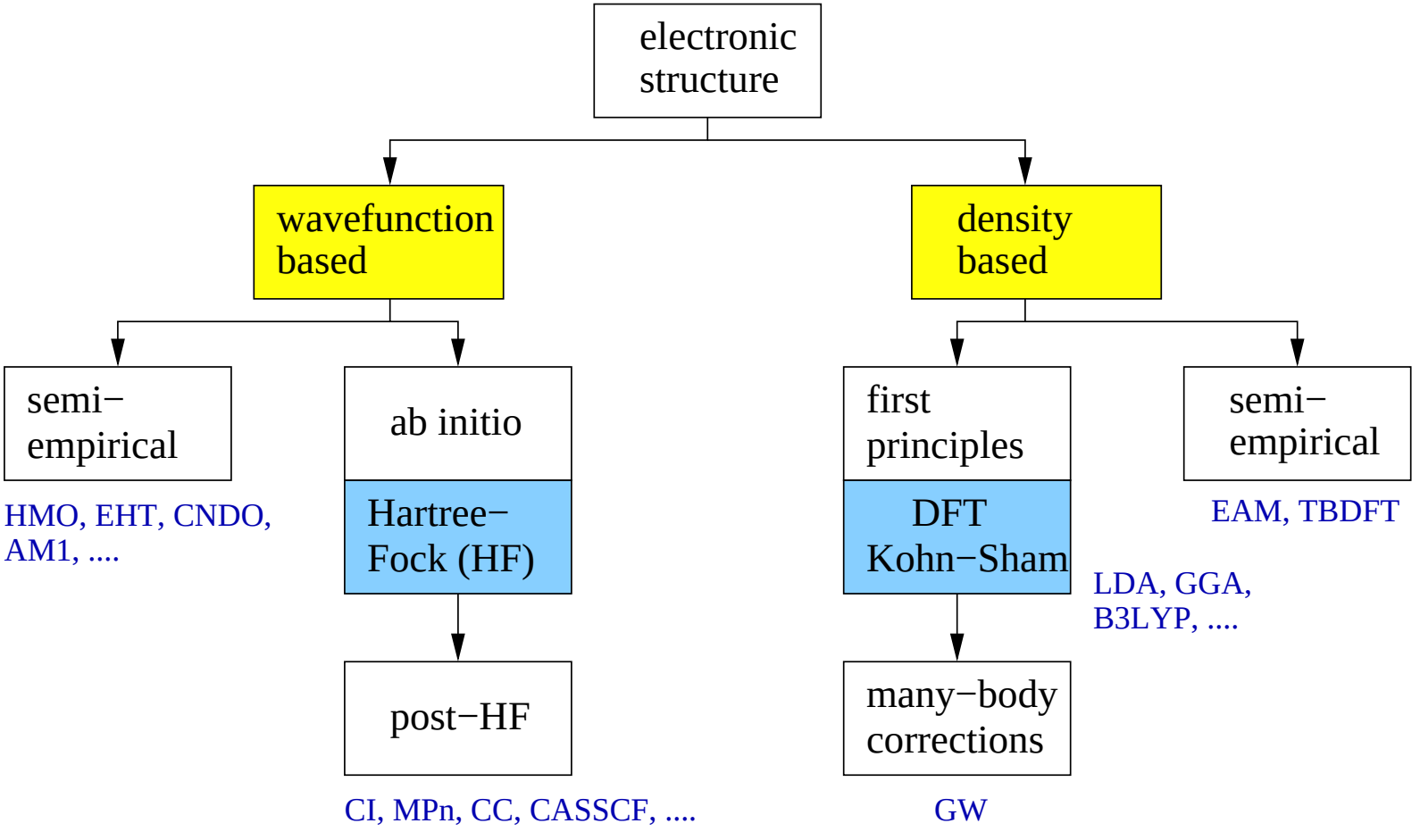
Electronic Schrödinger equation:

$$\hat{H}_{el}\Psi_{el,n}(r,R) = E_{el,n}(R)\ \Psi_{el,n}(r,R)$$

Potential energy surfaces:

$$V_n(R) = E_{el,n}(R) + V_{nuc,nuc}(R)$$

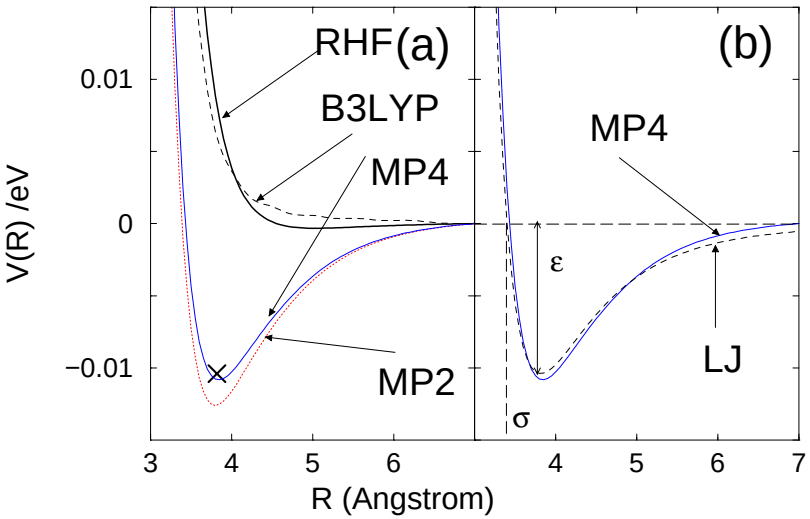
r = electronic, R = nuclear DOF, n = state, E_{el}= electronic energy, $V_{nuc,nuc}$ = nuclear repulsion



4.2 Electronic structure methods (cont'd)

(2) Dispersion forces and other non-bonded interactions

- **Potential curve of Ar-Ar**



- **Methods for non-bonded interactions**

rank	method	(type)	HB	CT	DI	WI	average
1	MPWB1K	(m-h-GGA)	0.61	0.50	0.52	0.22	0.46
2	MP2	(WFT)	0.66	0.60	0.55	0.16	0.49
16	B3LYP	(h-GGA)	0.77	0.80	0.78	0.60	0.74
31	PBE	(GGA)	0.50	2.94	0.49	0.28	1.05
44	SVWN5	(LDA)	4.63	6.73	2.93	0.40	3.67
	average		1.28	1.78	0.92	0.56	1.14

HB=H-bonded; CT=charge transfer; DI=dipolar interactions; WI=weak interactions; MAD (kcal/mol), 22 data sets; Truhlar JCTC **1**, 415 (2005)

- **The DFT+D method(s) for weak interactions**

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}$$

$$E_{\text{disp}} = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10} \cdots$$

Example: Grimme D2 correction

$$E_{\text{disp}}^{D2} = -s_6 \sum_{A}^{N_A} \sum_{B>A}^{N_A} \frac{C_6^{AB}}{R_{AB}^6} f_d(R_{AB})$$

Example: Dissociation energies (meV) of 2 graphene layers

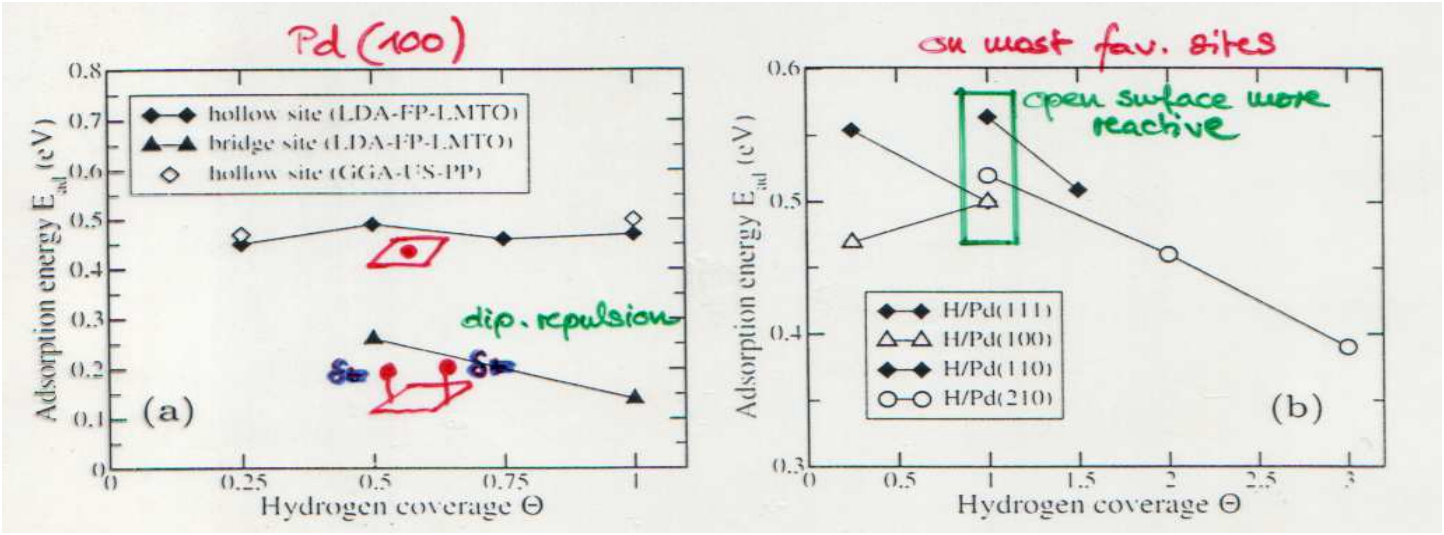
functional	DFT	DFT-D2	DFT-D3
BLYP	-29	62	59
RPBE	-31	65	55
PBE	-1	47	41
exp.		52 ± 5	

JCP **132**, 154104 (2010)

4.3 A few selected examples

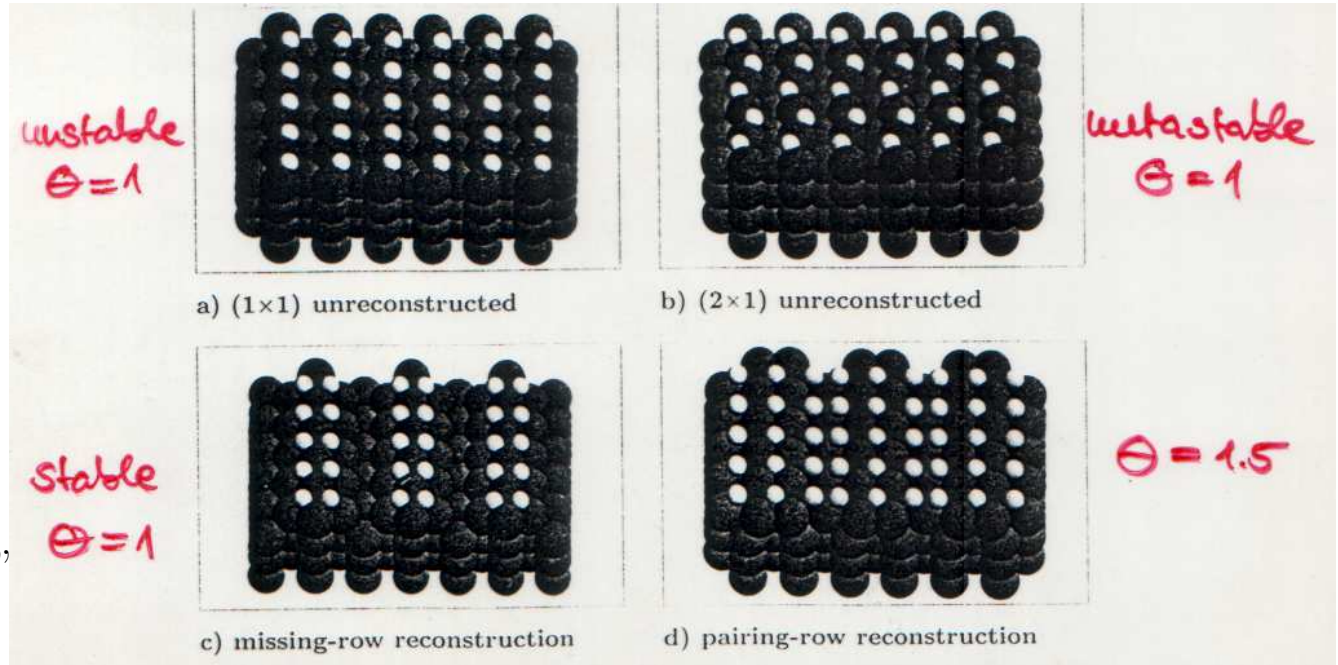
(1) H atoms at Pd low-index surfaces

- **Site, coverage, index dependence**



- **Surface reconstruction**

for H/Pd(100)



Groß, "Theoretical Surface Science"

4.3 A few selected examples (cont'd)

(2) Trends: Hammer-Nørskov model for adsorption on transition metals

- **Chemisorption energy: d-band contribution (atoms)**

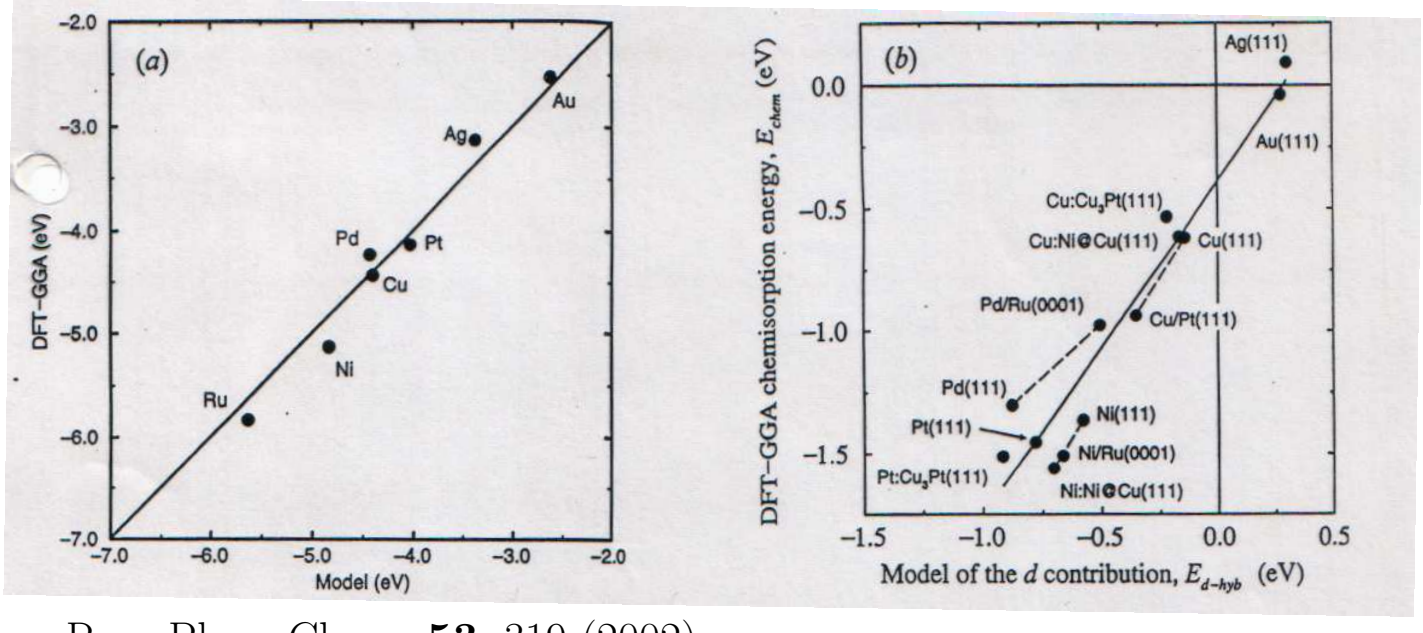
$$E_{d-hyb} = -2(1-f)\frac{V^2}{|\varepsilon_d - \varepsilon_a|} + \alpha V^2$$

f = d-band filling — V=coupling adsorbate level / d-band

$\varepsilon_{d,a}$ = d-band centre, adsorbate level — α = constant

- **First principles *vs.* model expression**

O adsorption — CO adsorption



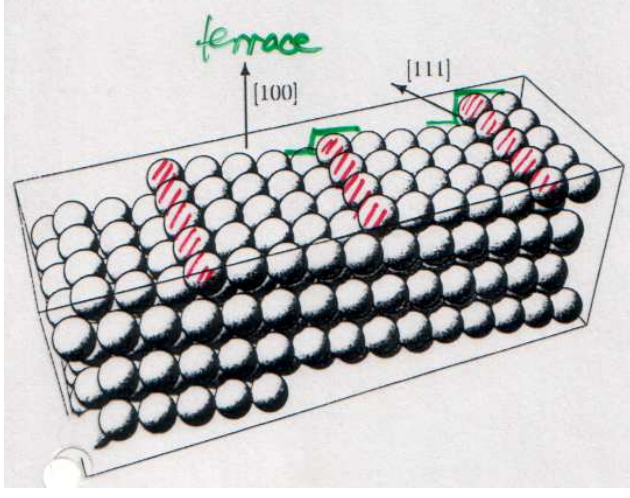
Ann. Rev. Phys. Chem. **53**, 319 (2002)

4.3 A few selected examples (cont'd)

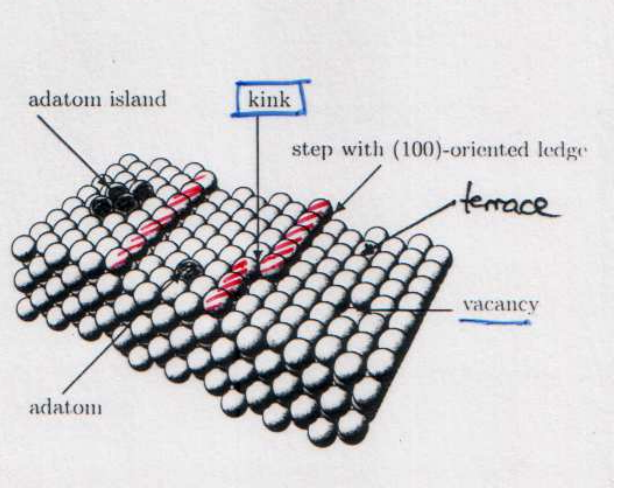
(3) Adsorption on structured surfaces

- **Stepped and structured surfaces**

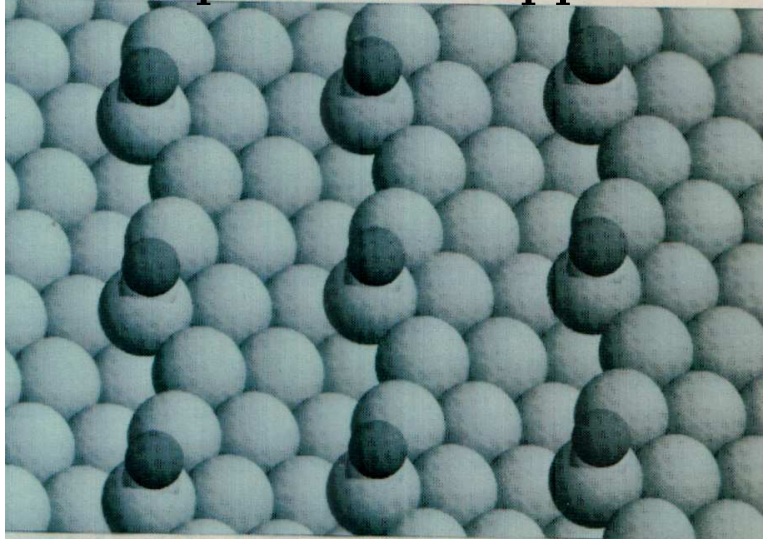
(911) surface



(755) surface



- **CO adsorption on stepped CO/Pt(11,7,5) kink sites**



ΔE_{ads}(Pt(11,7,5), Pt(111))$\sim$ 0.7 eV

defects / kinks are more reactive

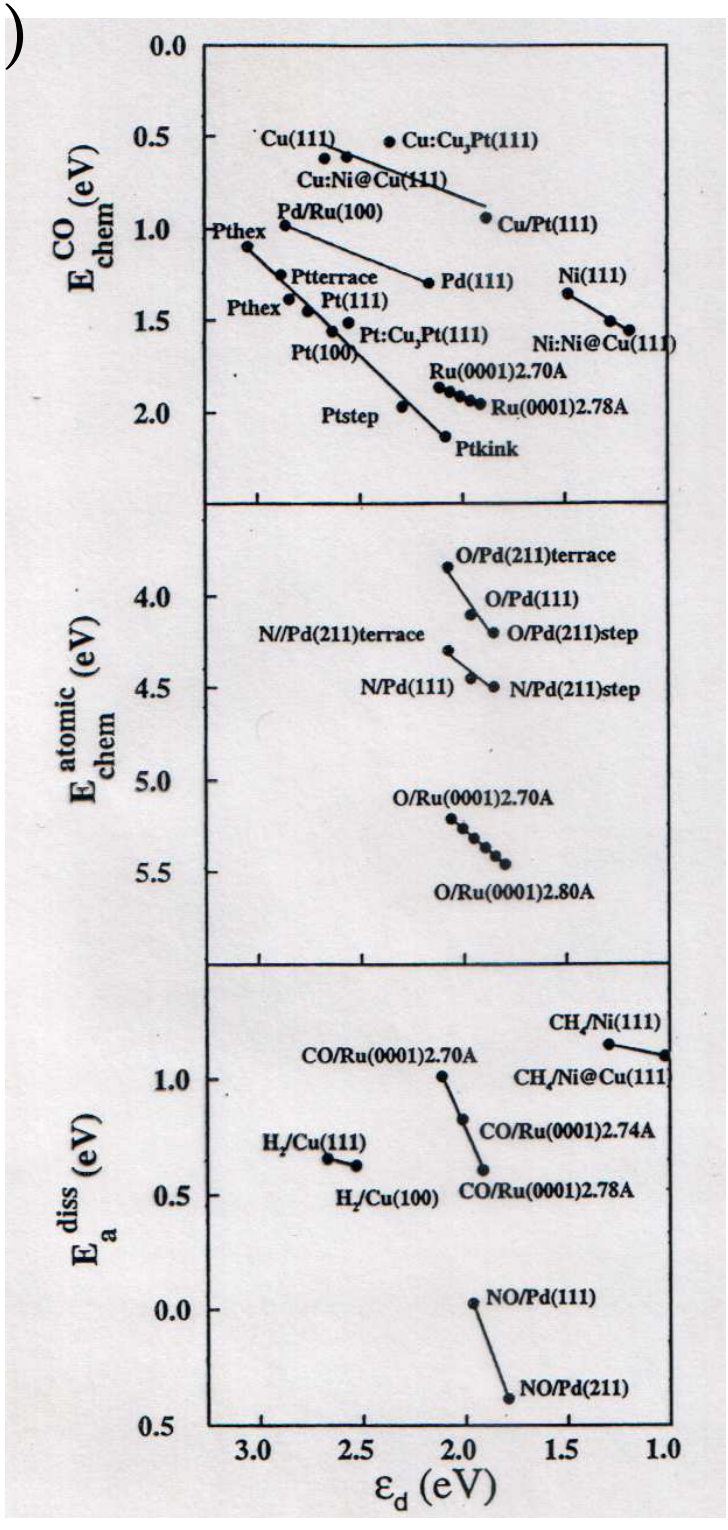
can be explained by d-band model

4.3 A few selected examples (cont'd)

(3) Adsorption on structured surfaces

- **Further examples**

Ann. Rev. Phys. Chem. **53**, 319 (2002)



4.3 A few selected examples (cont'd)

(4) Steps of ammonia synthesis

- **Reaction:**

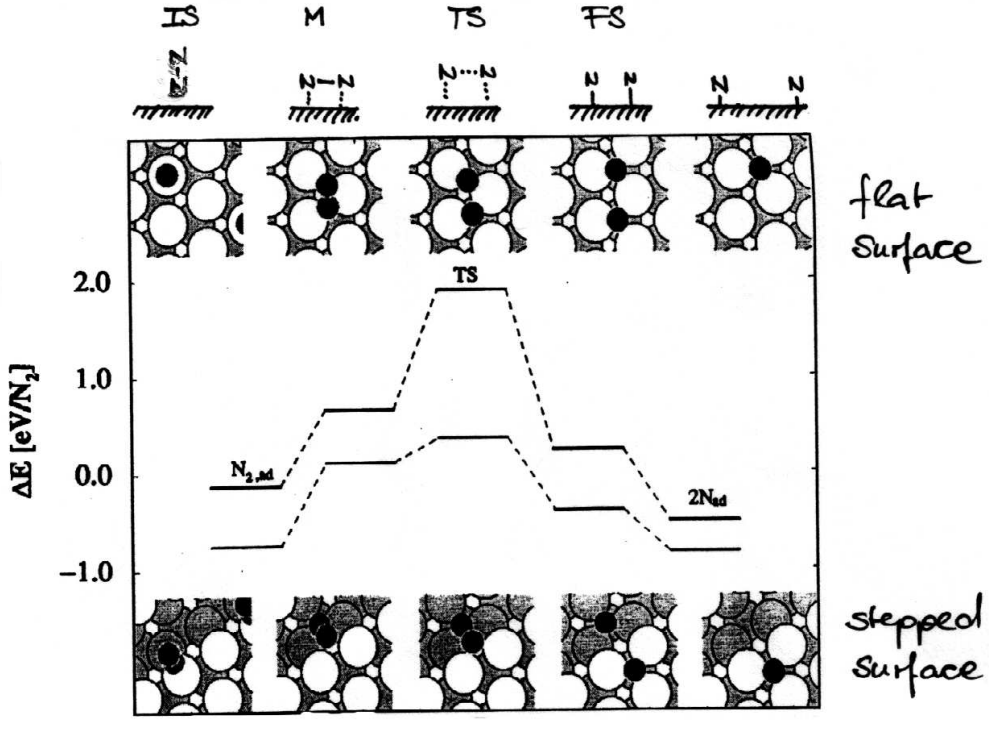
$$N_2 + 3\,H_2 \overset{\text{surface, p, T}}{\rightleftharpoons} 2\,NH_3$$

$N_2 + 2*$	$\longrightarrow$	$2N*$	(1)
$H_2 + 2*$	$\rightleftharpoons$	$2H*$	(2)
$N* + H*$	$\rightleftharpoons$	$NH* + *$	(3)
$NH* + H*$	$\rightleftharpoons$	$NH_2* + *$	(4)
$NH_2 + H*$	$\rightleftharpoons$	$NH_3* + *$	(5)
NH_3	$\rightleftharpoons$	$NH_3 + *$	(6)

$*$ = empty site on the surface

$\Longrightarrow$ step (1) is rate-limiting

- **Stationary points** for (1): N_2/Ru(0001)



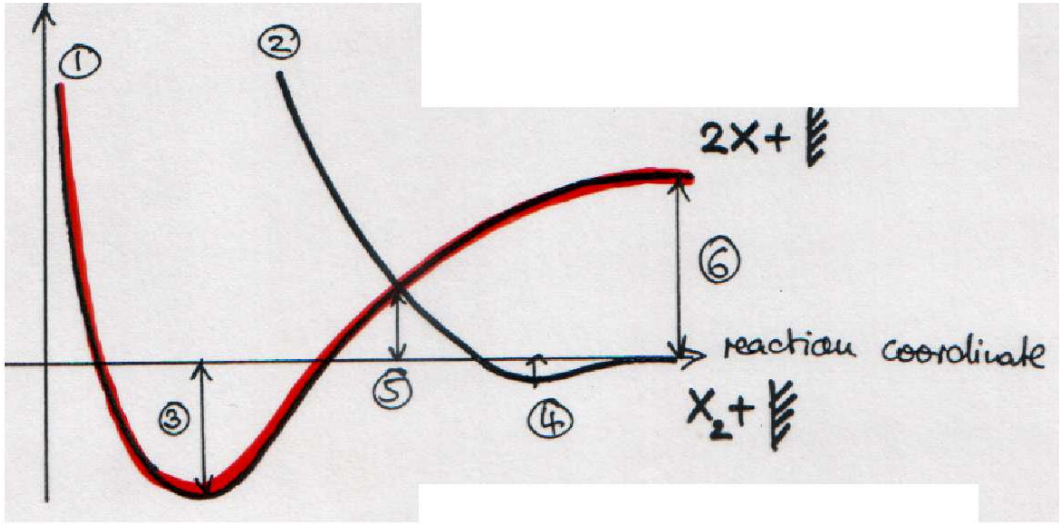
$\Longrightarrow$ reaction proceeds at steps

Nørskov *et al.*, Ann. Rev. Phys. Chem. **53**, 319 (2002)

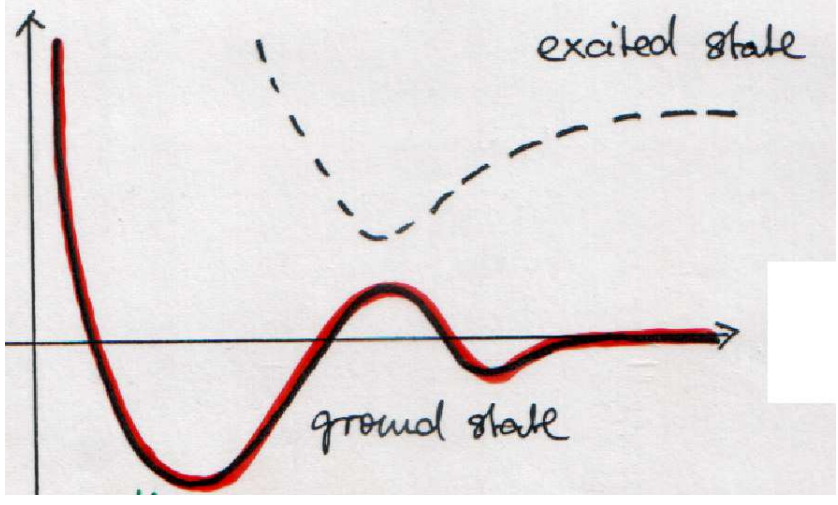
A few selected examples (cont'd)

(5) Activated, dissociative adsorption: Lennard-Jones picture

diabatic picture



adiabatic picture



❶ chemisorption curve
❷ physisorption curve
❸ chemisorption minimum
❹ physisorption minimum
❺ barrier to dissociation
❻ dissociation energy in gas phase

particles follow adiabatic potential

(if not too fast)

Summary and outlook

- **Summary**
  - Physisorption and chemisorption
  - Chemisorption: Affinity level matters
  - Chemisorption: (Metal) Fermi energy matters
  - Molecules: Molecular & dissociative adsorption
- **Outlook**
  - Potential energy surfaces
  - Reaction dynamics
  - Reaction kinetics
  - Heterogeneous catalysis