EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering
sunmil.epfl.ch

SuNMiL
Supramolecular NanoMaterials and Interfaces Laboratory

Electronic Properties of Surfaces
Lesson 13

MSE 304

Francesco Stellacci

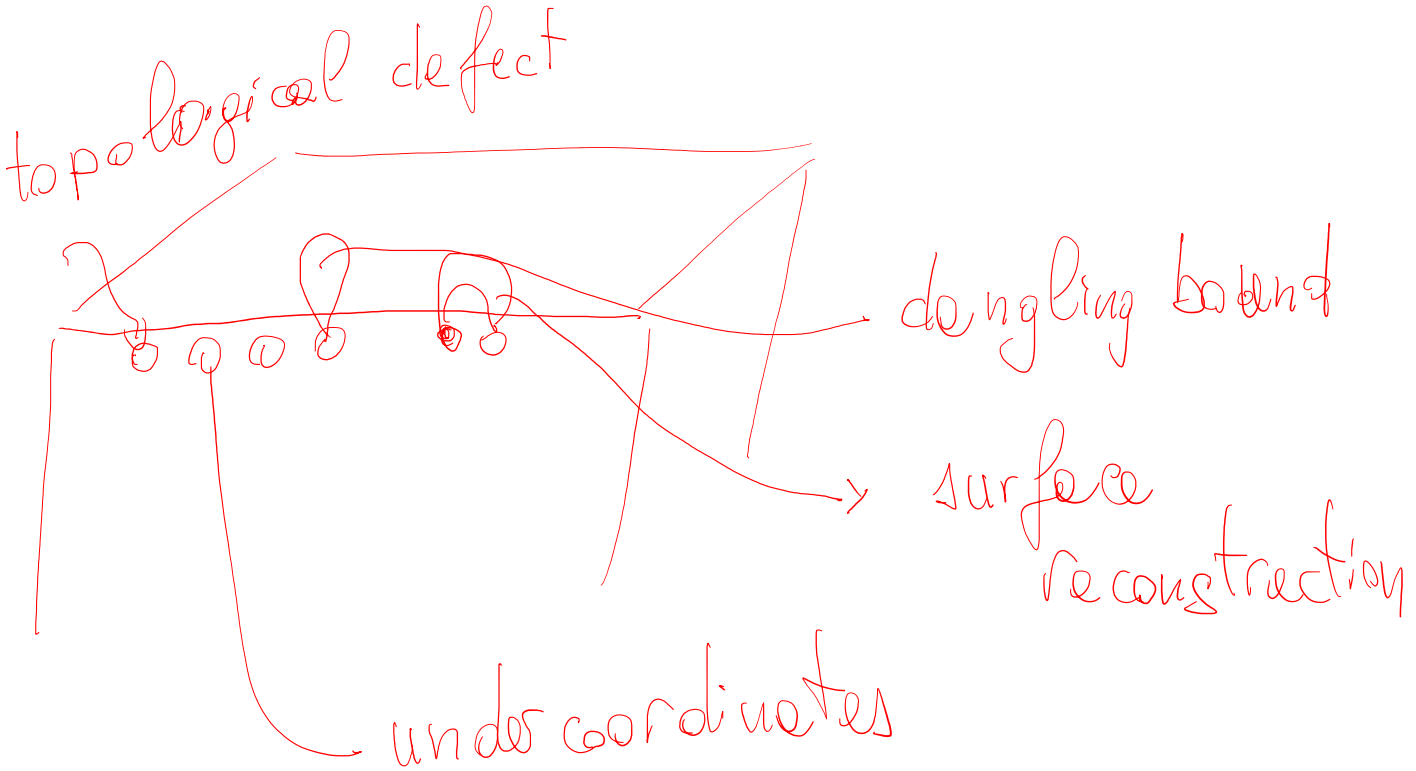
桑缪 썬밀 सानमिल ΣουNMιΛ سنمل СаНМПЛ

Reading for this Class

Chapter 5 and 6 of “Introduction to Surface Chemistry and Catalysis” by G. Samorjai

Key Topics from the Course

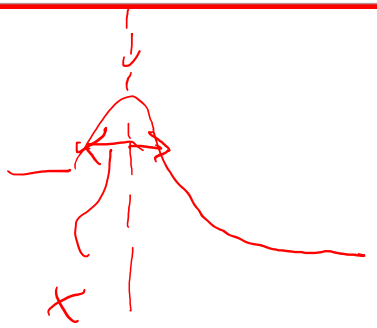
Concept of Surface



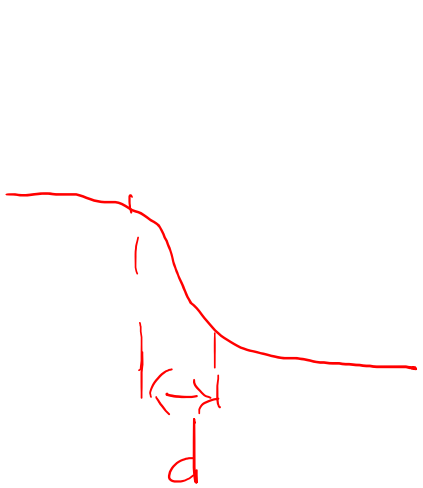
Key Topics from the Course

Diffuse Interfaces

Gibbs isotherm →



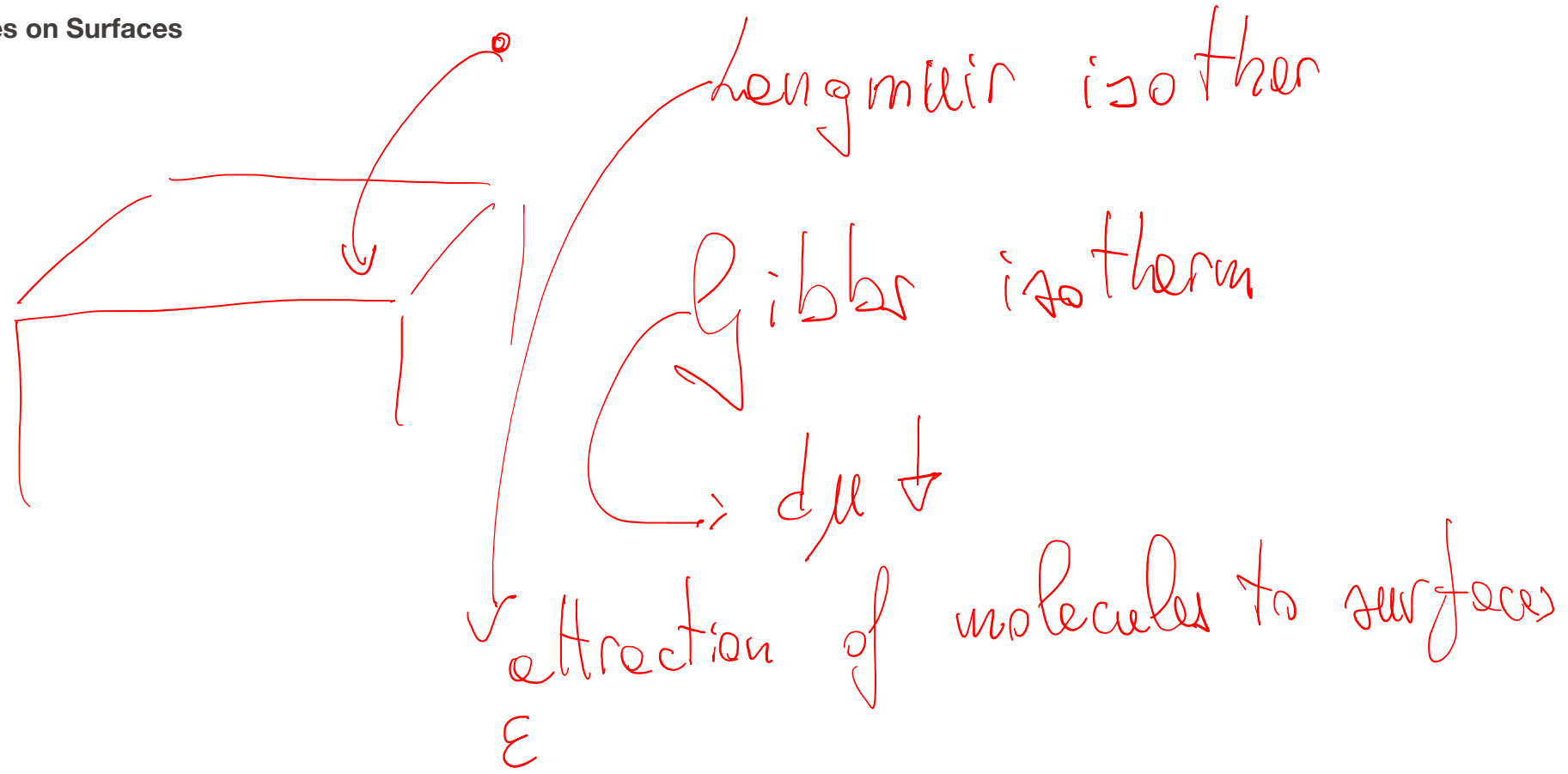
Cahn Hilliard →



→ as opposed to atomic

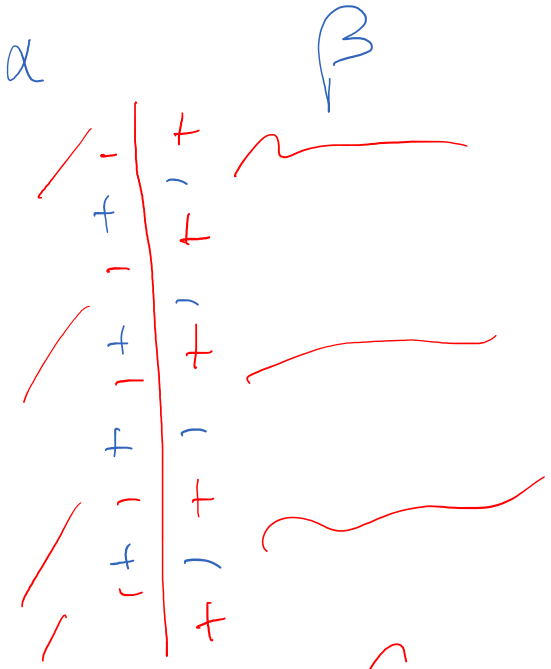
Key Topics from the Course

Adsorbates on Surfaces



Key Topics from the Course

Charged Interfaces



$$\mu_i^{\alpha} = \mu_i^{\beta} \quad \forall i$$

$$\mu_i^{\alpha} = \mu_i^{\circ} + RT \ln C_i + \text{?}$$

fluid

2 cases

charge

or

or

activity field

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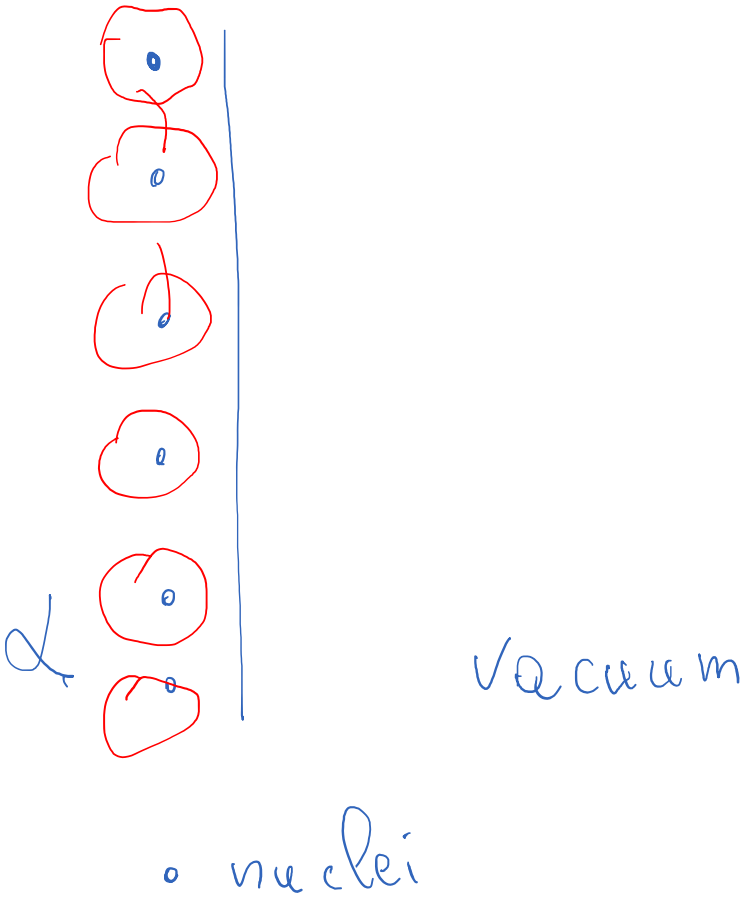
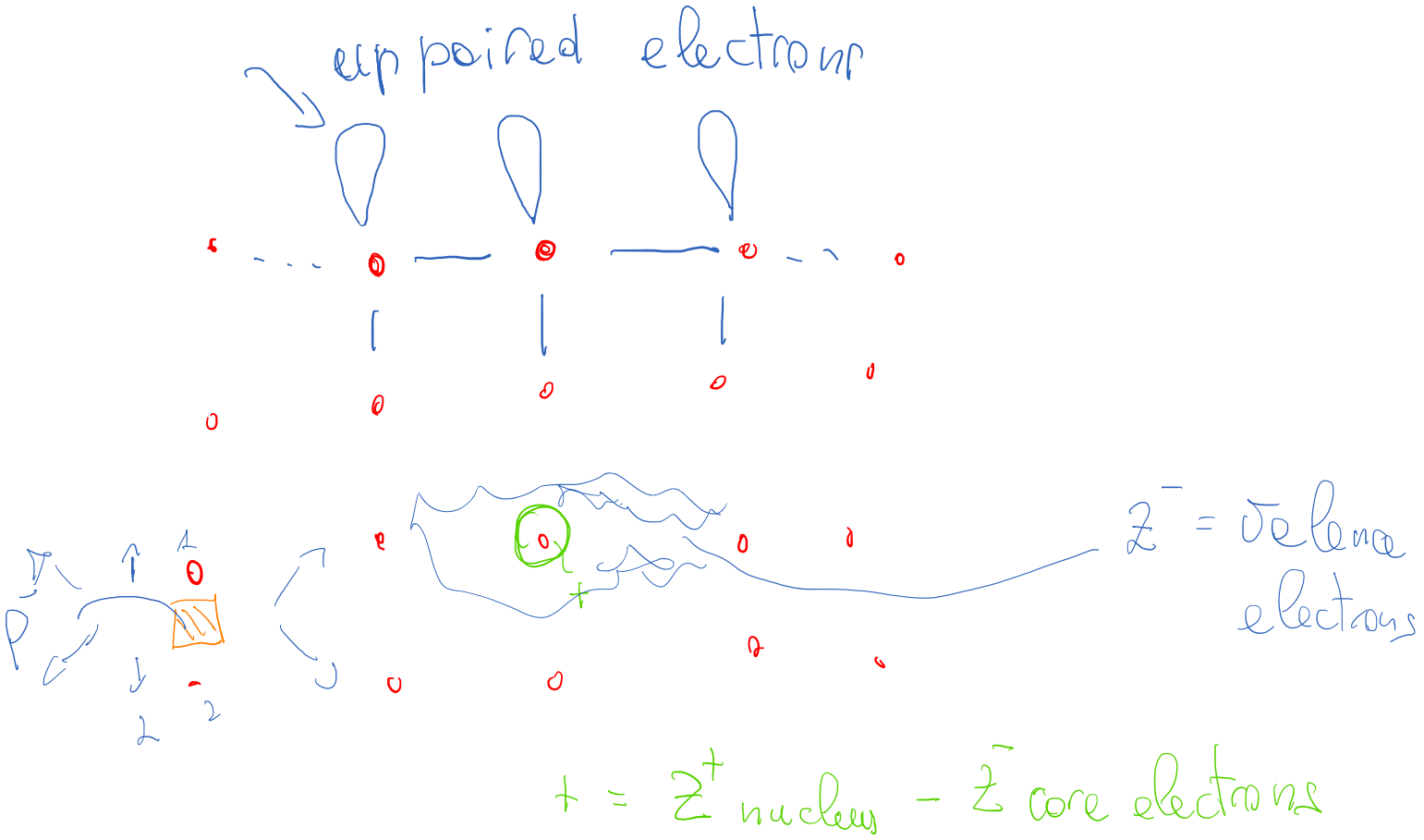
Content of this Class



Content of this Class



Solid State Electronic Description

atoms → the case of a crystal

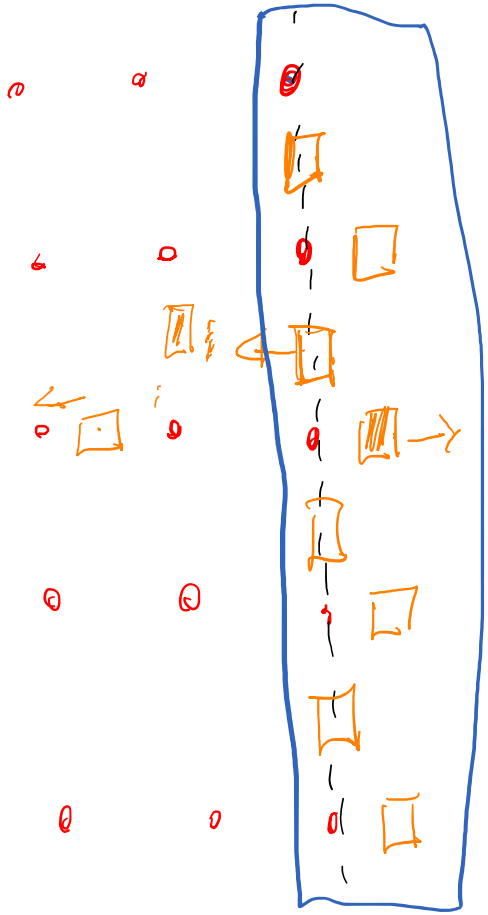
↓

nuclei are in crystallographic positions

Core electrons

→ valence electron will be involved in bond formation with positions that depend on the bond

Surface Electronic Description



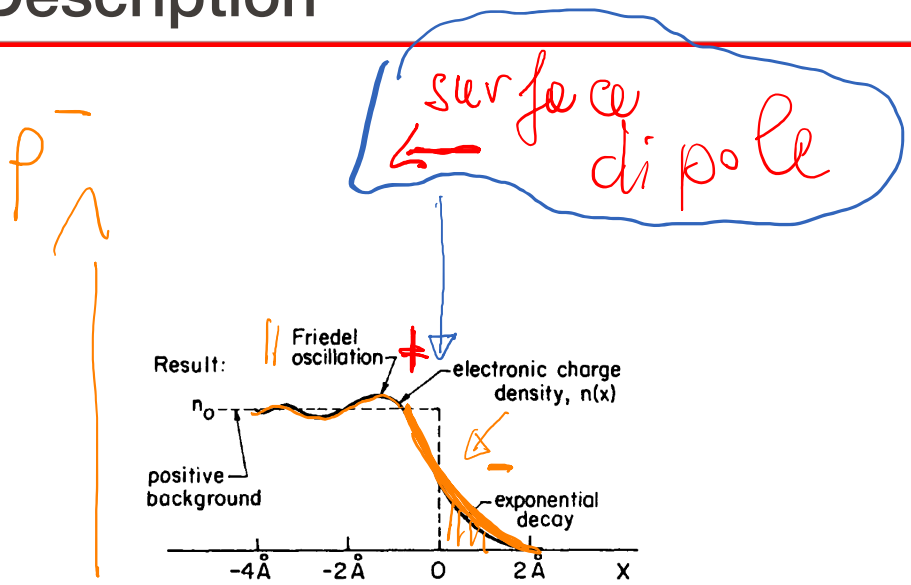


Figure 5.1. Schematic representation of the electronic charge density distribution at a metal surface.

every surface has an associated dipole

Charge Density at Interfaces

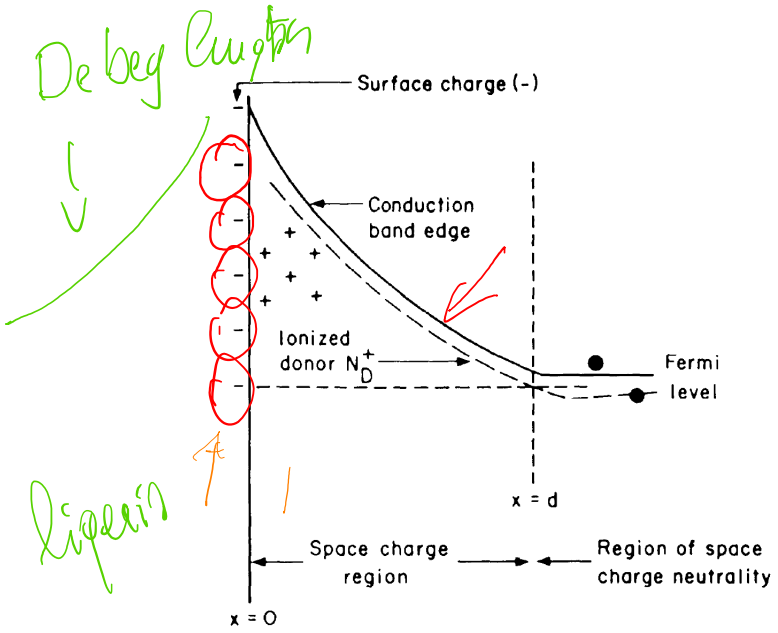


Figure 5.2. Scheme of space-charge buildup at an *n*-type semiconductor surface upon adsorption of electron acceptor molecules.

$$\frac{d^2V}{dx^2} = -\frac{\rho_e(x)}{\epsilon\epsilon_0} \longrightarrow V(x) = -\frac{e}{2\epsilon\epsilon_0} N_D^+ (x-d)^2$$

$x=0$

$$V_s = \frac{e}{2\epsilon\epsilon_0} N_D^+ d^2$$

electroneutrality

$$en_e^{bulk} d \approx eN_D^+ d$$

$$d = \left[\frac{2\epsilon\epsilon_0 V_s}{en_e^{bulk}}\right]^{1/2}$$

Debey length

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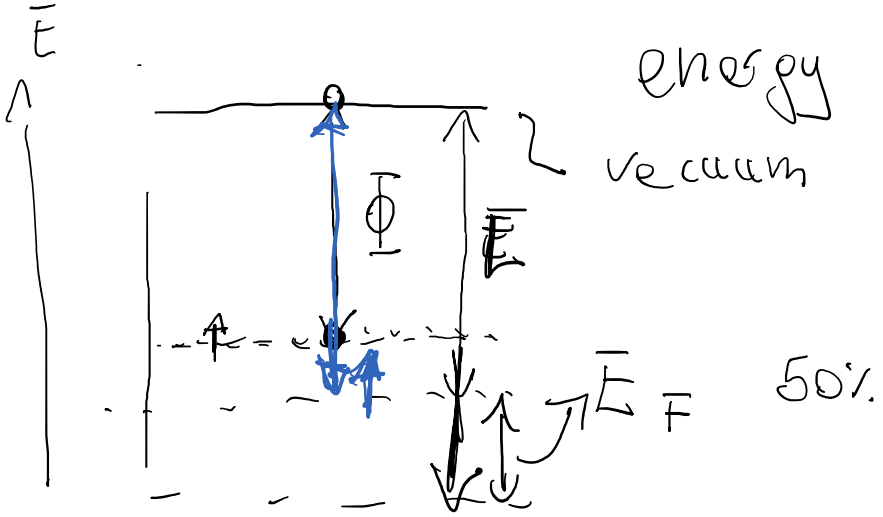
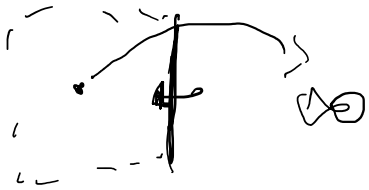
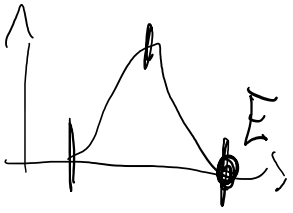
The Work Function

Φ → minimal energy need to extract an electron from the material to ∞ [the vacuum] with 0 kinetic energy



$\Phi = E_{vac} - E_F$





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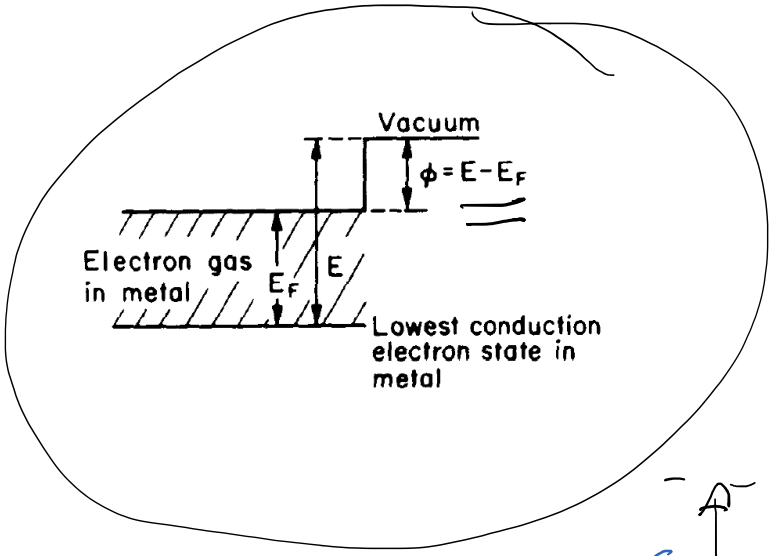
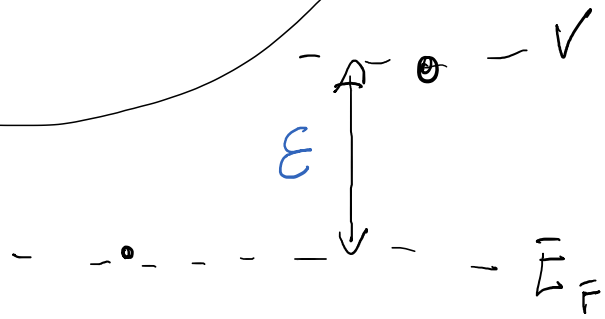
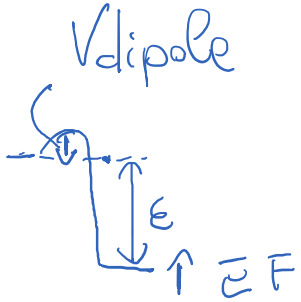
The Work Function in a Realistic Sample



$$e\phi = eV_{\text{exchange}} + eV_{\text{dipole}} - E_F$$





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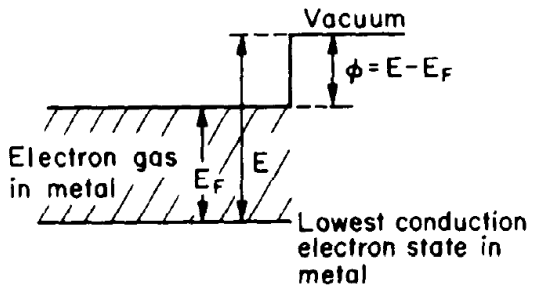
The Work Function in a Realistic Sample



$$e\phi = eV_{\text{exchange}} + eV_{\text{dipole}} - E_F$$

property of the material

property of the surface

Dependence on Facets

because of different bonding and bonding density

Dependence on Size

$\mu = \mu^{\infty} + f(N)$

E_F depends on size

Dependence on Roughnes

$\sum \uparrow = \uparrow$

$\sum eV_{dip}$

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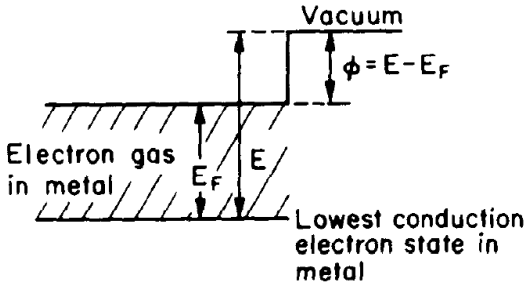
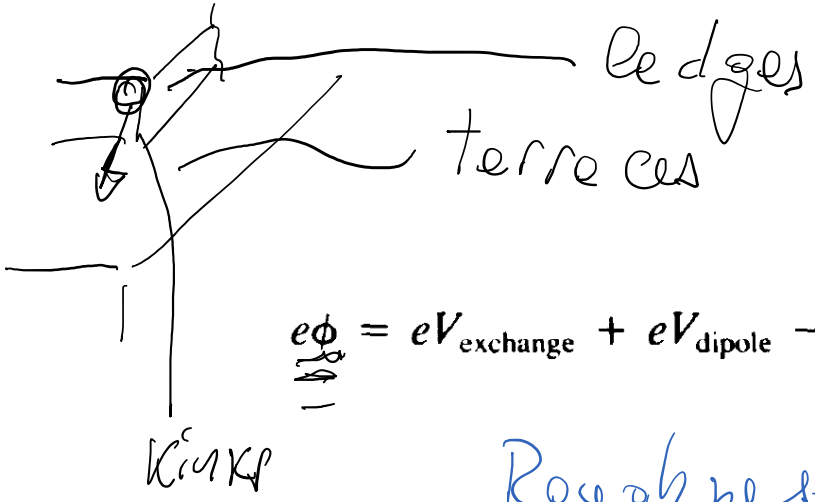
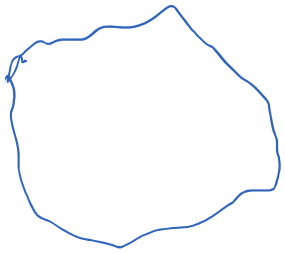
The Work Function in a Realistic Sample



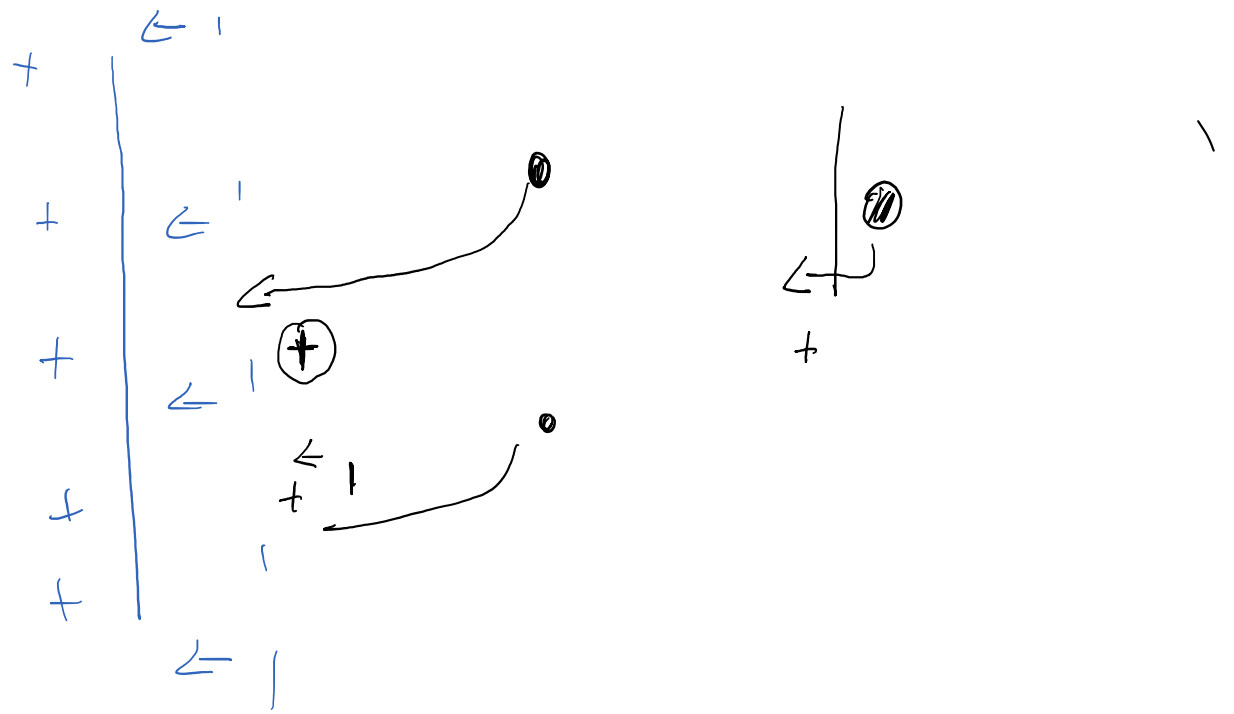


$$e\phi = eV_{\text{exchange}} + eV_{\text{dipole}} - E_F$$



Roughness
Size
impurities

Adsorption at Surfaces: Charge Transfer



Adsorption at Surfaces: Charge Transfer

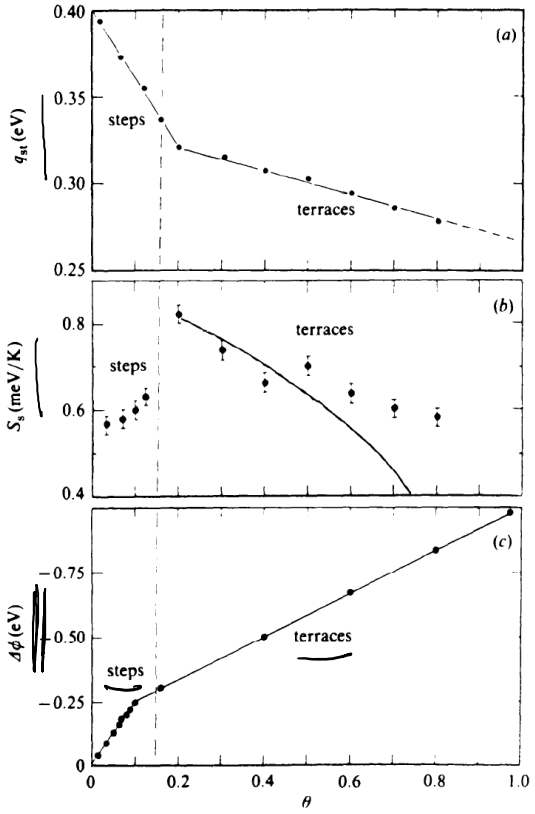
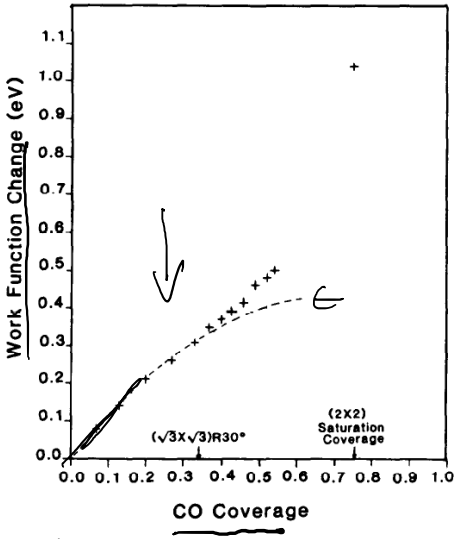


Figure 5.6. The enthalpy change **(a)**, the entropy **(b)**, and the work function change **(c)** for xenon adsorption as a function of xenon coverage on the Pd(810) stepped crystal surface [53].

Work Function and Adsorption

$\Phi \propto E_F - e V_{dipole}$



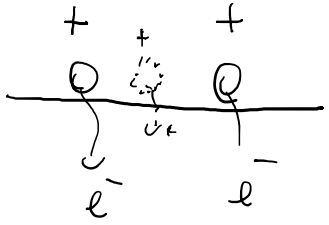


Figure 5.7. The change of work function of Rh(111) upon CO adsorption as a function of coverage [54].

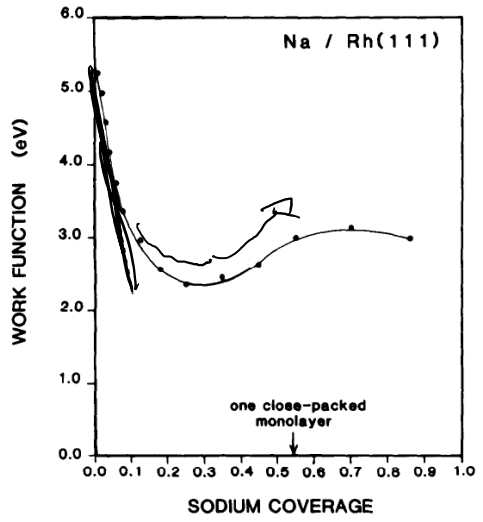


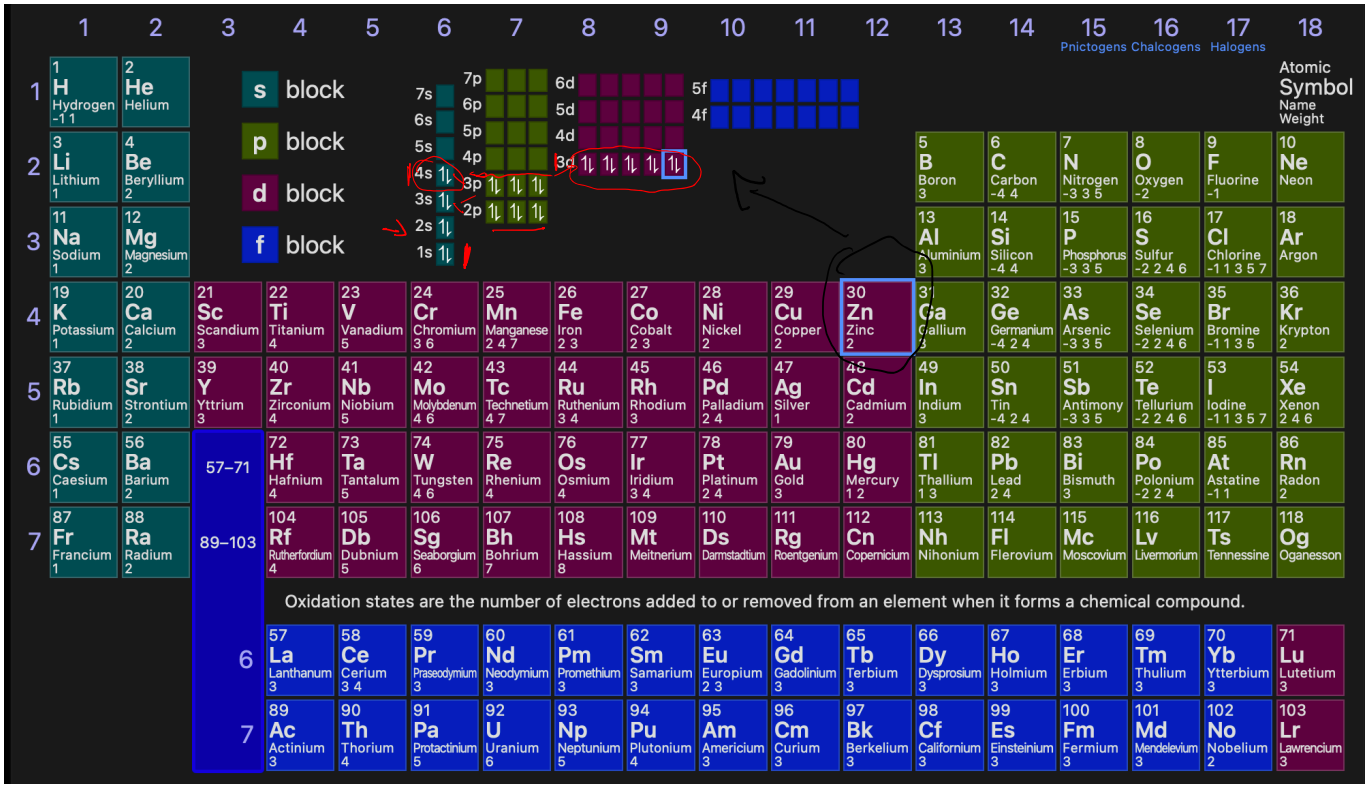
Figure 5.8. The change of work function of Rh(111) upon adsorption of sodium as a function of Na coverage [54].

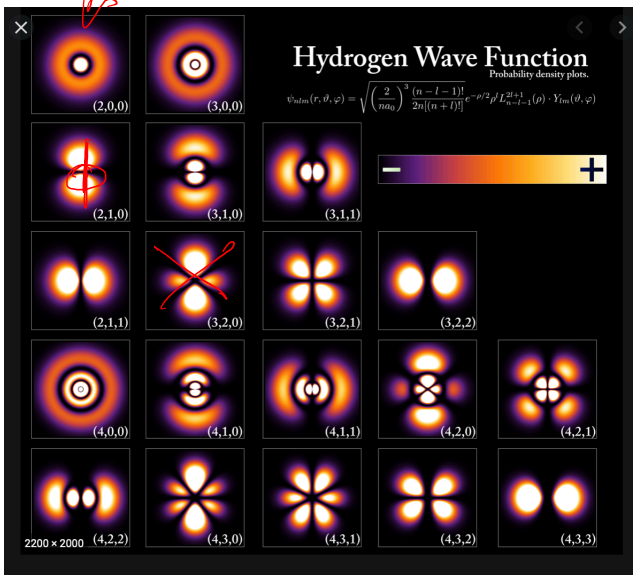
Adsorption vs Absorption

Adsorption on surface → physisorption
↳ charge transfer

Absorption ou surfaces → chemisorption
↓
geometrically defined
interaction
?

The Periodic Table





https://ptable.com/?lang=en#Electrons

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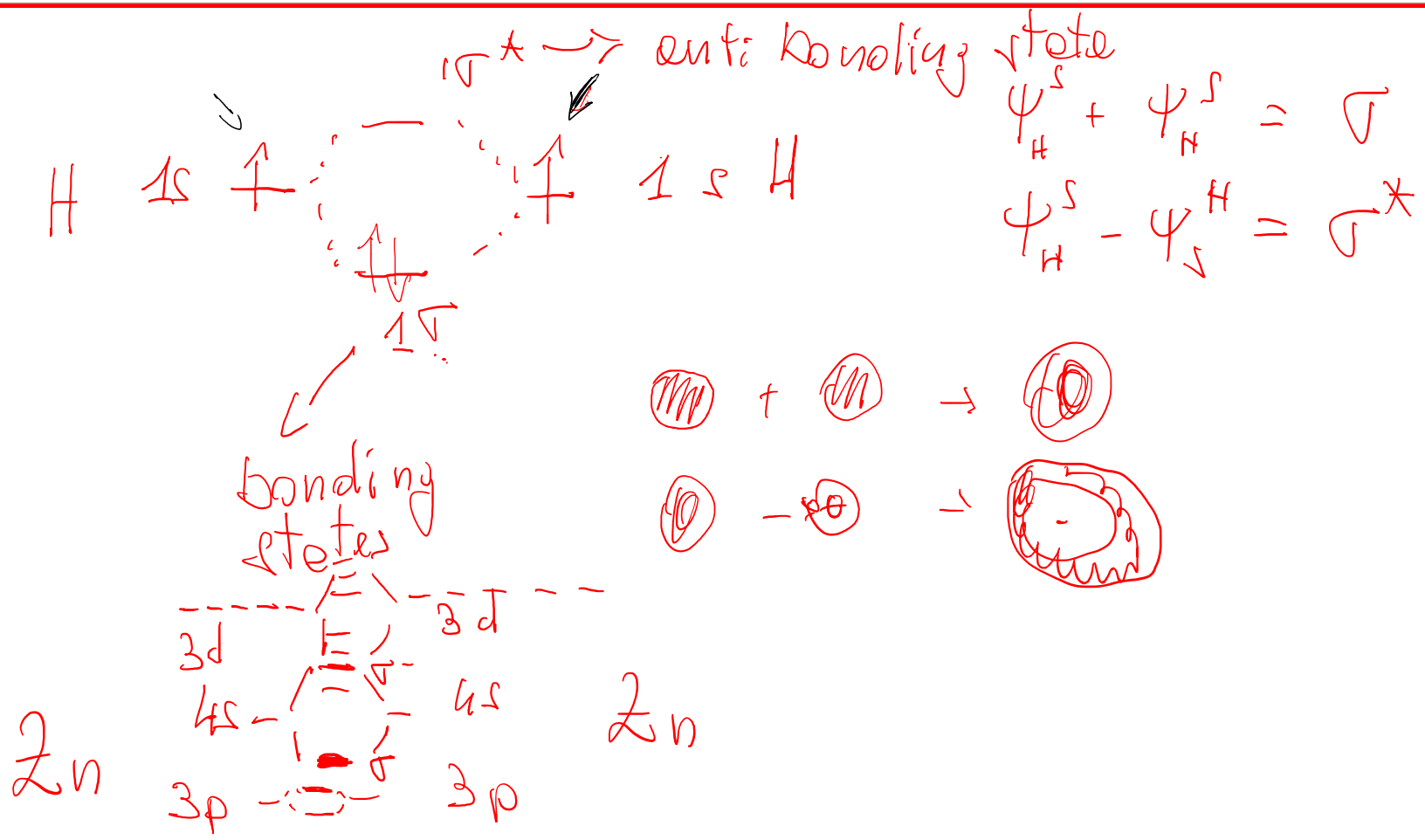
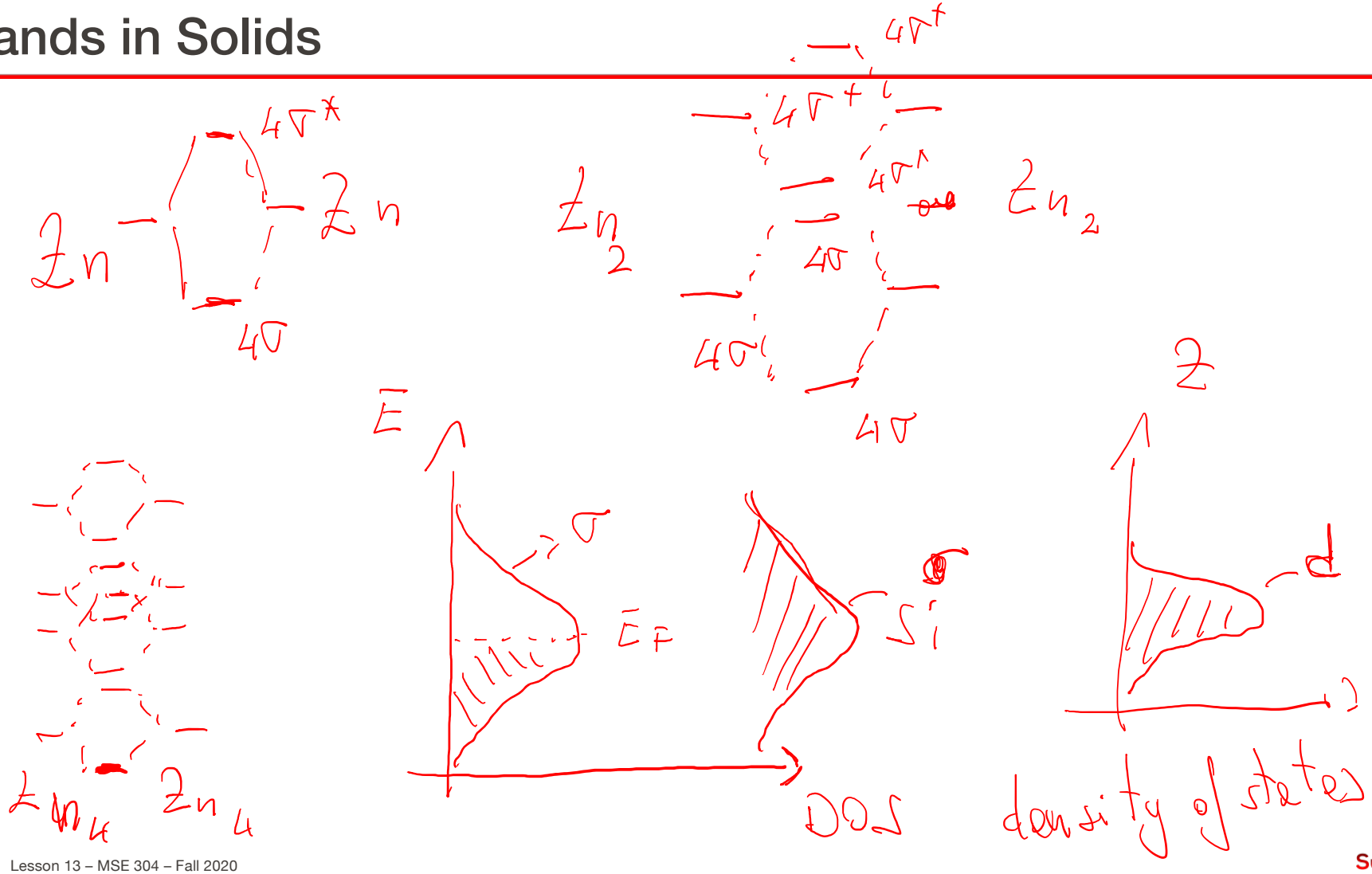
The Molecular Orbital Theory



Bands in Solids



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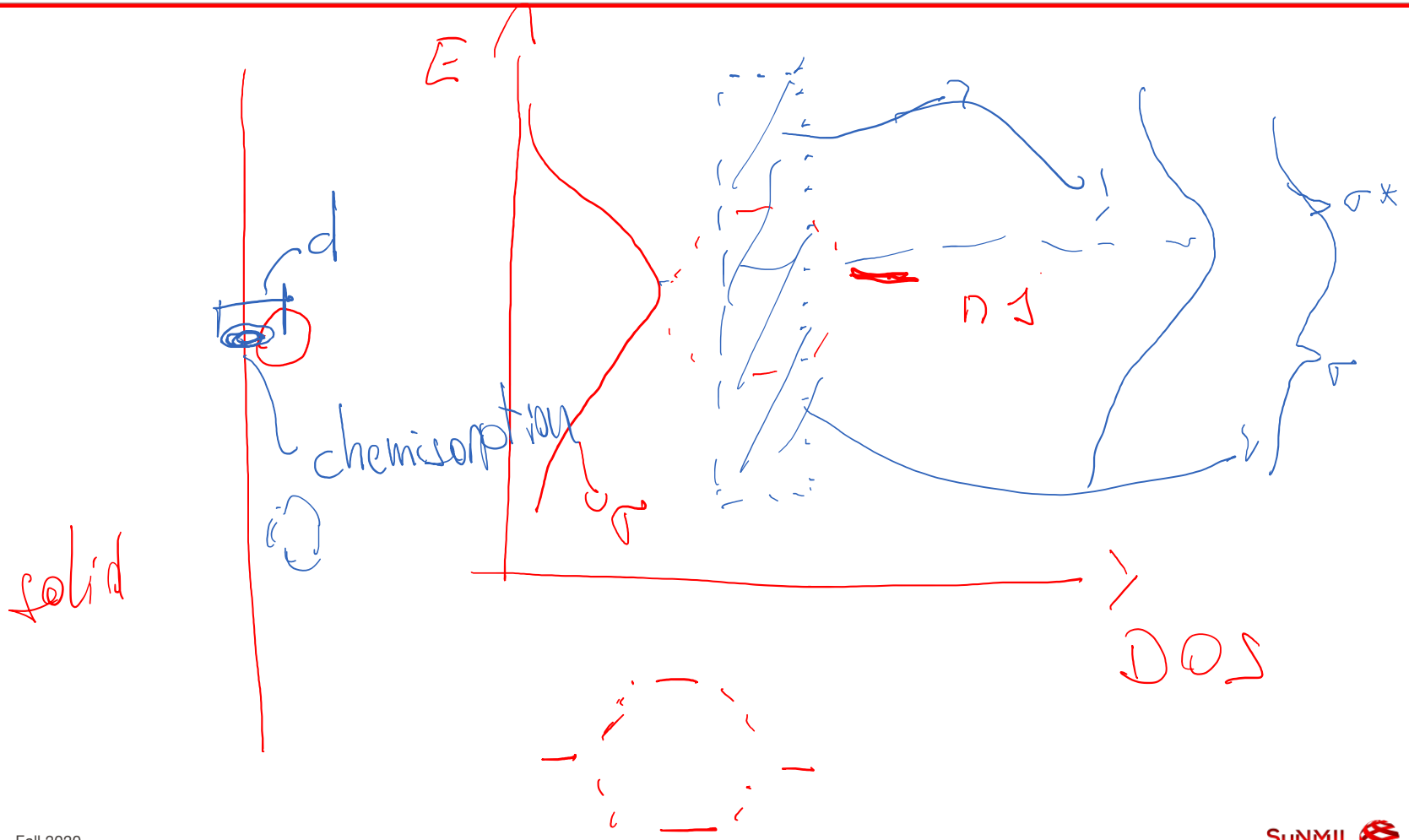
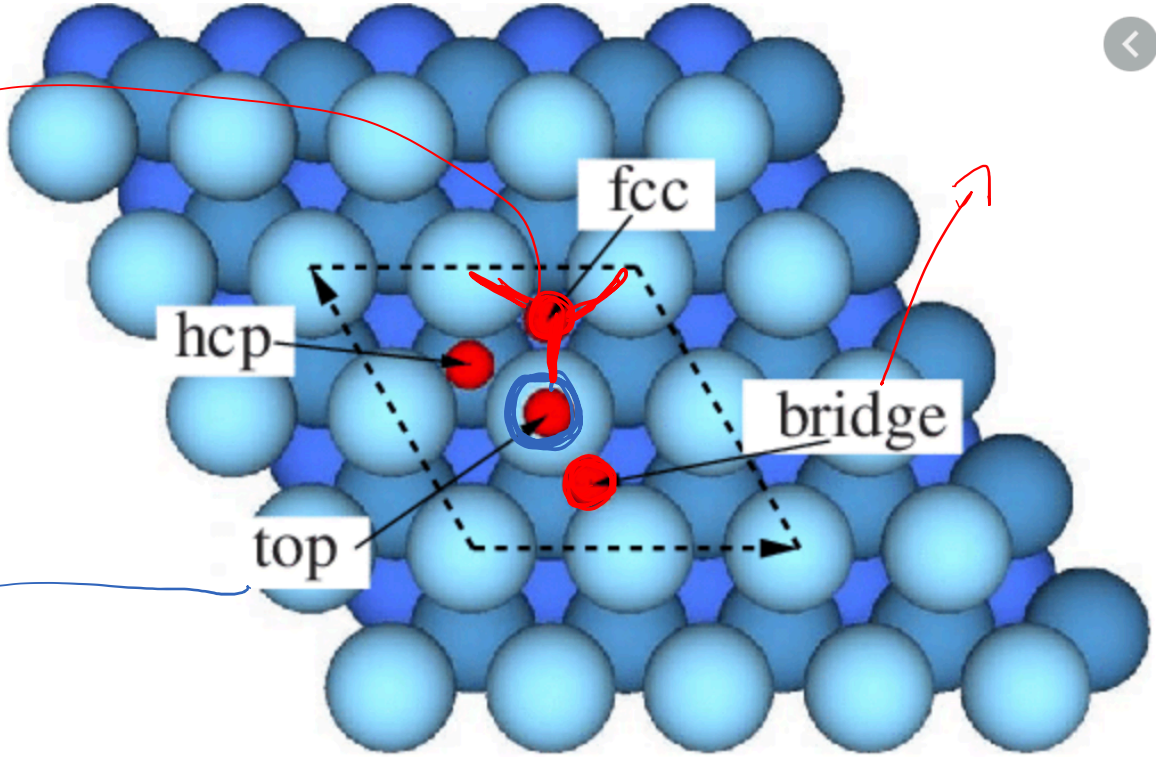
Absorption on Solids



Absorption Geometry



The Chemical Bond

H_2

O_2

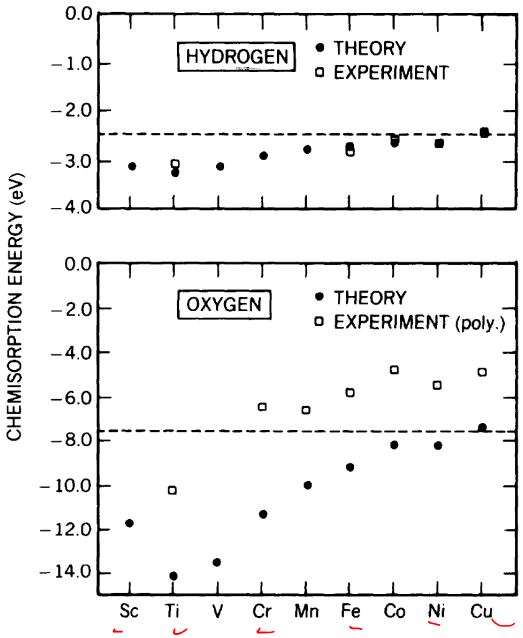
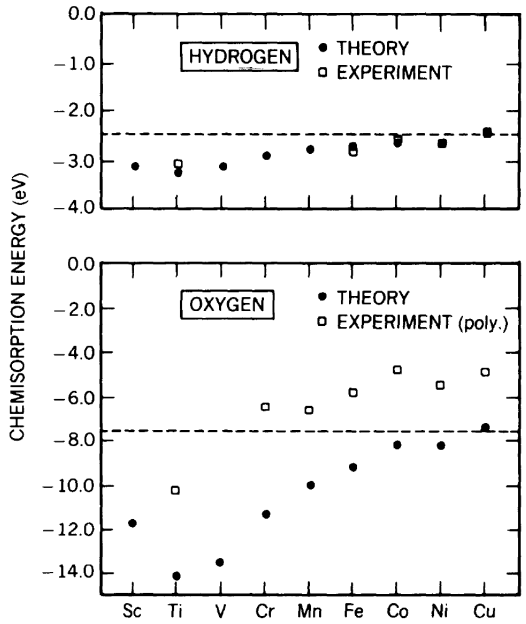


Figure 6.1. Chemisorption energies of hydrogen and oxygen on transition metals across the periodic table that were calculated using the effective-medium theory and also measured on polycrystalline surfaces [23].

bonding formed with the d atoms

The Chemical Bond



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The Chemical Bond

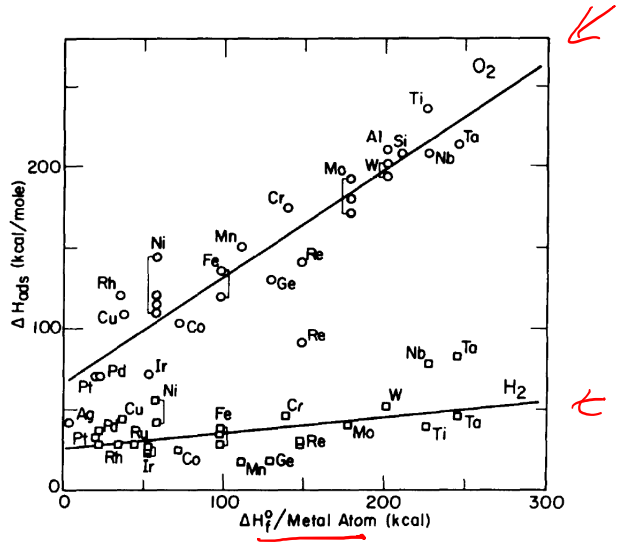

Figure 6.2. Heats of adsorption of O_2 and H_2 on various transition metals as a function of the heats of formation of the corresponding oxides and hydrides (per metal atom) [2].

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The Chemical Bond

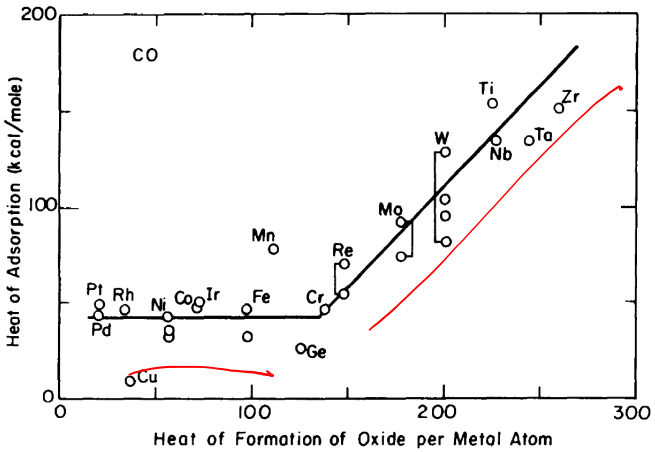
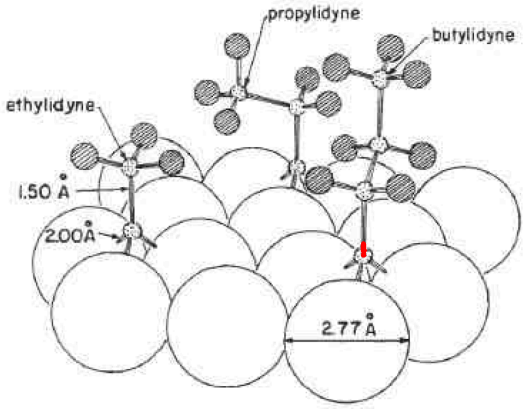


Figure 6.3. Heats of adsorption of CO on various transition metals as a function of the heats of formation of the corresponding oxides (per metal atom) [2].

The Chemical Bond



Pt (111) + ethylidyne, propylidyne and butylidyne

symmetry

specific geometry

The Chemical Bond- Absorption on Surfaces

Langmuir isotherm
Gibbs isotherm
$d\mu$

↓

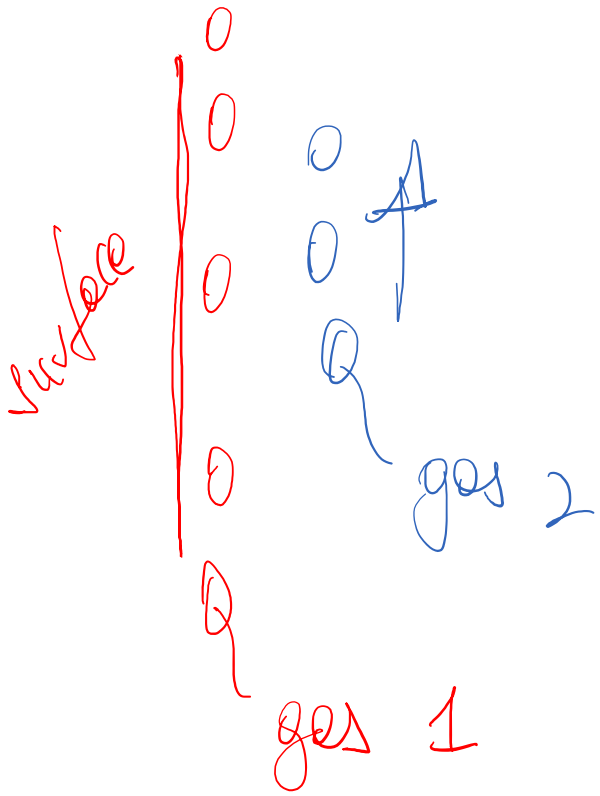
bonding
absorbate
surface

why do different molecules absorb differently on different surfaces

formation of specific bond

bond materials most of the difference

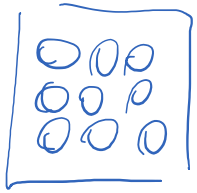
Gas Separation

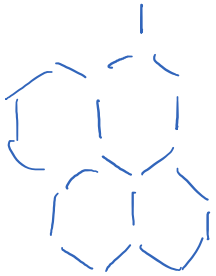


Materials with high Surface Area to Volume Ratio

very porous

- zeolites
- covalent organic frameworks





Conclusions

Surface are intrinsically dipolar

they form bond

↳ the driver for absorption