Chapter 5 Computational design of catalytic materials
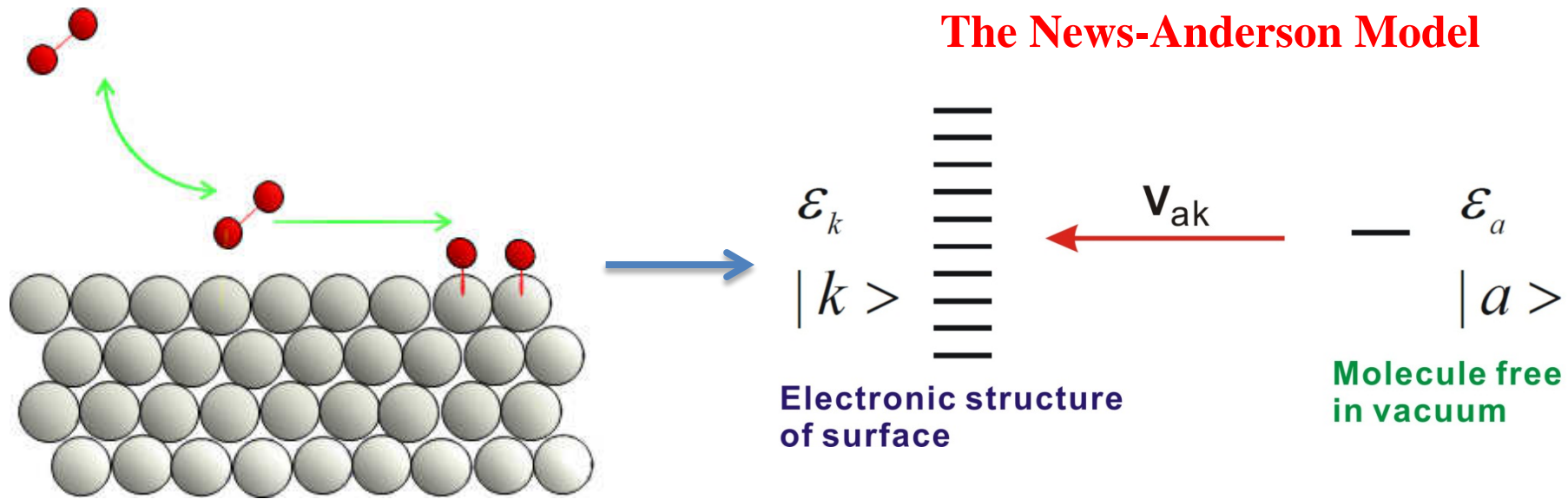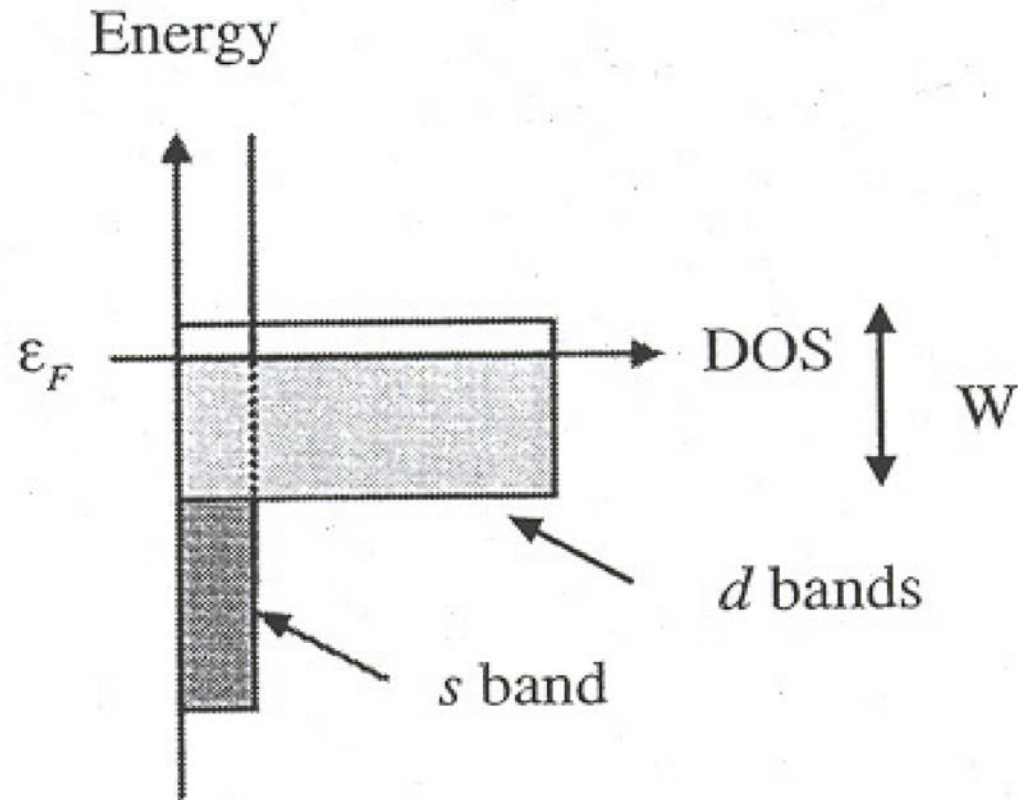
- An introduction to catalysis and surface chemistry
- *d*-Band theory of catalysis
- Photocatalysis and plasmon-enhanced catalysis

The Adsorbed System

The News-Anderson Model

ε_k

$|k>$

V_{ak}

ε_a

$|a>$

Electronic structure of surface

Molecule free in vacuum

$$H = E_a c^+{}_a \, c_a + \sum_{k \in bands} E_k c^+{}_k \, c_k + \left\{ \sum_k V_{ak} c^+{}_a \, c_k + h.c. \right\}$$

The density of state for a transition metal System

Theoretical Formalism of the Adsorbed System

Based on the principle of density functional theory, the total energy of the system can be found as

$$E[n_\alpha, V_{eff}{}^\alpha] = \sum_i \varepsilon_i{}^\alpha [V_{eff}{}^\alpha] - \int V_{eff}{}^\alpha n_\alpha d^3r + F[n_\alpha]$$

where $\qquad n_\alpha = \sum_{i \in occ} |\Psi_i{}^\alpha|^2 \qquad$ with $\qquad [-\frac{1}{2}\nabla^2 + V_{eff}{}^\alpha] \Psi_i{}^\alpha = \varepsilon_i{}^\alpha \Psi_i{}^\alpha$

$F[n_\alpha]$: energy functional, comprising of the energy terms due to Hartree, ionic, and exchange-correlation interactions.

The subscript α refers to an atom/molecule (A) free in vacuum, a substrate (M), and the resulting adsorbed system (A+M).
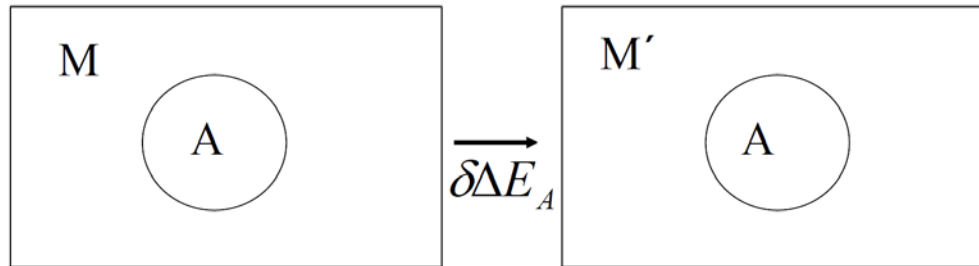
The energy variation due to δn_α and $\delta V_{eff}{}^\alpha$ becomes

$$\delta E = E\left(n_0 + \delta n, V_{eff} + \delta V_{eff}\right) - E\left(n_0, V_{eff}\right)$$
$$+ O(\delta n^2, \delta V_{eff}{}^2, \delta n \delta V_{eff})$$

Theoretical Formalism of the Adsorbed System

The adsorption energy of A+M can be determined by

$$\Delta E_{ads} = E_{tot}(A + M) - E_{tot}(A) - E_{tot}(M)$$

Consider the case of the same adsorbate on different substrates. The lowest order change in interaction energy with M replaced by M' can be found as

$$\delta[\Delta E_{ads}] = \delta\left[\Delta\left(\sum_{i \in occ} \varepsilon_i\right)\right] + \int \delta V_{eff}(M \to M') \cdot \delta n_A$$

Theoretical Formalism of the Adsorbed System

From the News-Anderson model, the adsorbed system can be described by $H|l> = \varepsilon_l|l>$

The set of energy eigenfunctions $\{|l>\}$ can be expressed as a linear combination of $|a> \; and \; \{|k>\}$: $|l> = c_{al}|a> + \sum_k c_{kl}|k>$

The Green function $G(\varepsilon) = \sum_l \frac{|l><l|}{\varepsilon+i\gamma-\varepsilon_l}$ is the solution of

$(\varepsilon + i\gamma - H)G(\varepsilon) = I$ (I is a unit matrix), which has a matrix form of

$$\begin{bmatrix} \varepsilon + i\gamma - \varepsilon_a & -V_{k1\,a} & -V_{k2\,a} & \cdots \\ -V_{a\,k1} & \epsilon + i\gamma - \varepsilon_{k1} & 0 & \cdots \\ -V_{a\,k2} & 0 & \varepsilon + i\gamma - \varepsilon_{k2} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} G_{aa} & G_{a\,k1} & \cdots \\ G_{k1\,a} & G_{k1\,k1} & 0 \\ G_{k2\,a} & 0 & \cdots \\ \vdots & \vdots & \vdots \end{bmatrix} = I \;,$$

which gives $(\varepsilon + i\gamma - \varepsilon_a)G_{aa} - \sum_k V_{ak}G_{ka} = 1$

$(\varepsilon + i\gamma - \varepsilon_k)G_{ka} - V_{ka}G_{aa} = 0$ for all $k \in \{k_1, k_2, \dots\}$

$$G_{aa}(\varepsilon) = \frac{1}{\varepsilon+i\gamma-\varepsilon_a-\sum_k\frac{V_{ak}V_{ka}}{(\varepsilon+i\gamma-\varepsilon_k)}}$$

Theoretical Formalism of the Adsorbed System

The adsorbate-projected density of state (LDOS) can then be determined:

$$n_a(\varepsilon) = \sum_l |< l|a >|^2 \delta(\varepsilon - \varepsilon_l) =$$

$$-\frac{1}{\pi}\sum_l |< l|a >|^2 \, Im\left[\frac{1}{\varepsilon+i\gamma-\varepsilon_l}\right] = -\frac{1}{\pi}Im\left[\sum_l \frac{<a|l><l|a>}{\varepsilon+i\gamma-\varepsilon_l}\right] =$$

$$-\frac{1}{\pi}Im[G_{aa}]$$

Here $G_{aa}(\varepsilon) = \left[\frac{1}{(\varepsilon-\varepsilon_a+\Lambda(\varepsilon)+i\Delta(\varepsilon))}\right]$ with

$$\Delta(\varepsilon) = -Im\left[\sum_k \frac{|V_{ak}|^2}{(\varepsilon+i\gamma-\varepsilon_k)}\right] = \pi\sum_k|V_{ak}|^2\delta(\varepsilon - \varepsilon_k) \text{ and}$$

$$\Lambda(\varepsilon) = Re\left[\sum_k \frac{|V_{ak}|^2}{(\varepsilon+i\gamma-\varepsilon_k)}\right] = \frac{1}{\pi}P\int\frac{\Delta(\varepsilon')}{\varepsilon-\varepsilon\prime}d\varepsilon'$$

Theoretical Formalism of the Adsorbed System

➤ To calculate $G_{aa}(\varepsilon)$, we first project $\{|k>\}$ onto the localized basis $\{|l>\}$: $|k> = \sum_l |l><l|k>$.

➤ We can then derive

$$\Delta(\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k) =$$

$$\pi \sum_k \sum_{ll'} <k|l><l|V|a><a|V|l'><l'|k> \delta(\varepsilon - \varepsilon_k)$$

● **_Adsorbate couples to a narrow d-band of the substrate_**

Let a–orbital of the adsorbate only couples to a narrow d-band of the substrate, $\Delta(\varepsilon) = \pi|V_{ad}|^2 \sum_k |<k|d>|^2 \delta(\varepsilon - \varepsilon_k) = \pi|V_{ad}|^2 \delta(\varepsilon - \varepsilon_d)$ and

$$\Lambda(\varepsilon) = \frac{1}{\pi} P \int \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' = \frac{V_{ad}^2}{\varepsilon - \varepsilon_d}, \text{ resulting in}$$

$$G_{aa}(\varepsilon) = \left[\frac{1}{(\varepsilon - \varepsilon_a + \Lambda(\varepsilon) + i\Delta(\varepsilon))}\right] = \frac{\varepsilon - \varepsilon_d + i\gamma}{(\varepsilon - \varepsilon_a)(\varepsilon - \varepsilon_d + i\gamma) - V_{ad}^2} = \frac{\varepsilon - \varepsilon_d + i\gamma}{(\varepsilon + i\gamma - \varepsilon_+)(\varepsilon + i\gamma - \varepsilon_-)}$$

with $\varepsilon_+ = \bar{\varepsilon} - \sqrt{V_{ad}^2 + \bar{\varepsilon}^2}$, $\varepsilon_- = \bar{\varepsilon} + \sqrt{V_{ad}^2 + \bar{\varepsilon}^2}$, and $\bar{\varepsilon} = (\varepsilon_a + \varepsilon_d)/2$
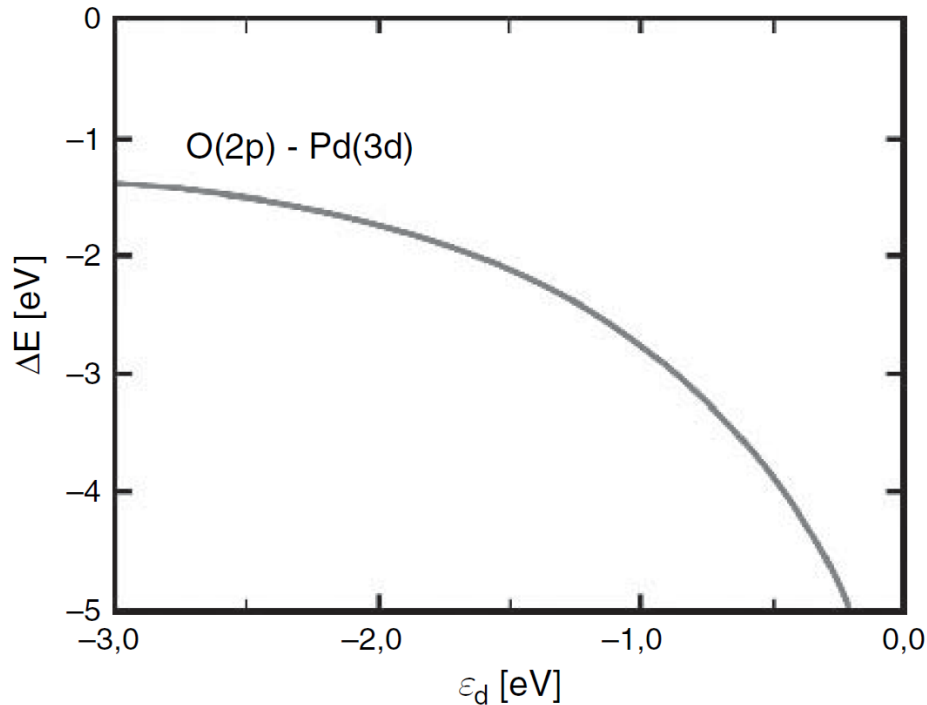
Theoretical Formalism of the Adsorbed System

- *Adsorbate couples to a narrow d-band of the substrate*
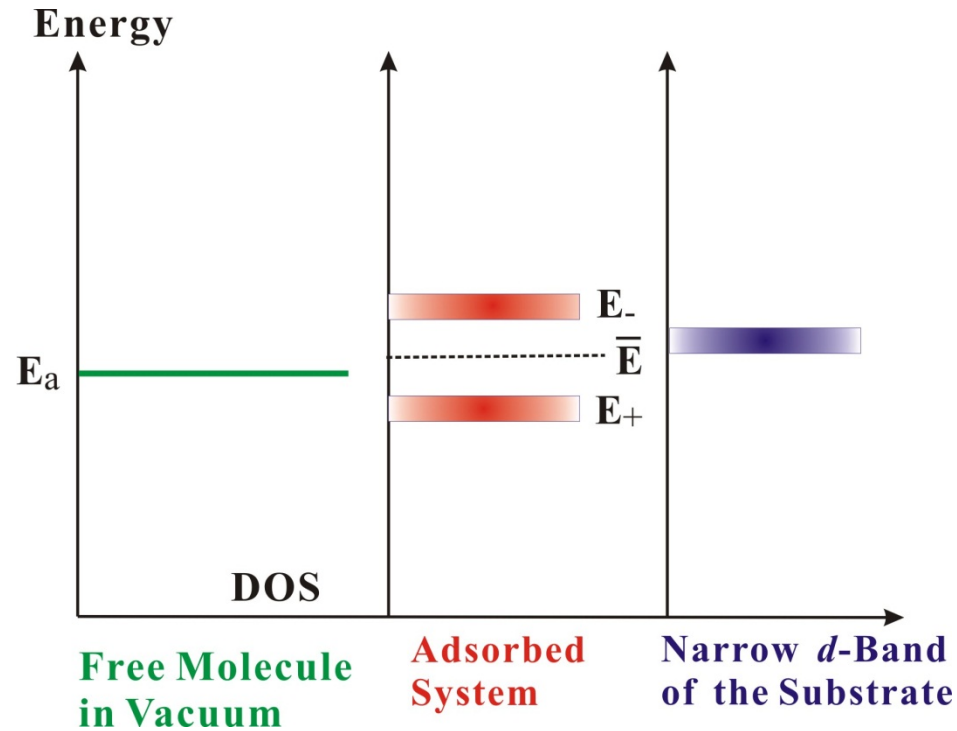
Theoretical Formalism of the Adsorbed System

- **_Adsorbate couples to a narrow d-band of the substrate_**

$$\Delta E_{ads} = E_{tot}(A + M) - E_{tot}(A) - E_{tot}(M)$$

$$= \sum_{l \in occ} \varepsilon_l - \sum_{k \in occ} \varepsilon_k - \varepsilon_a$$

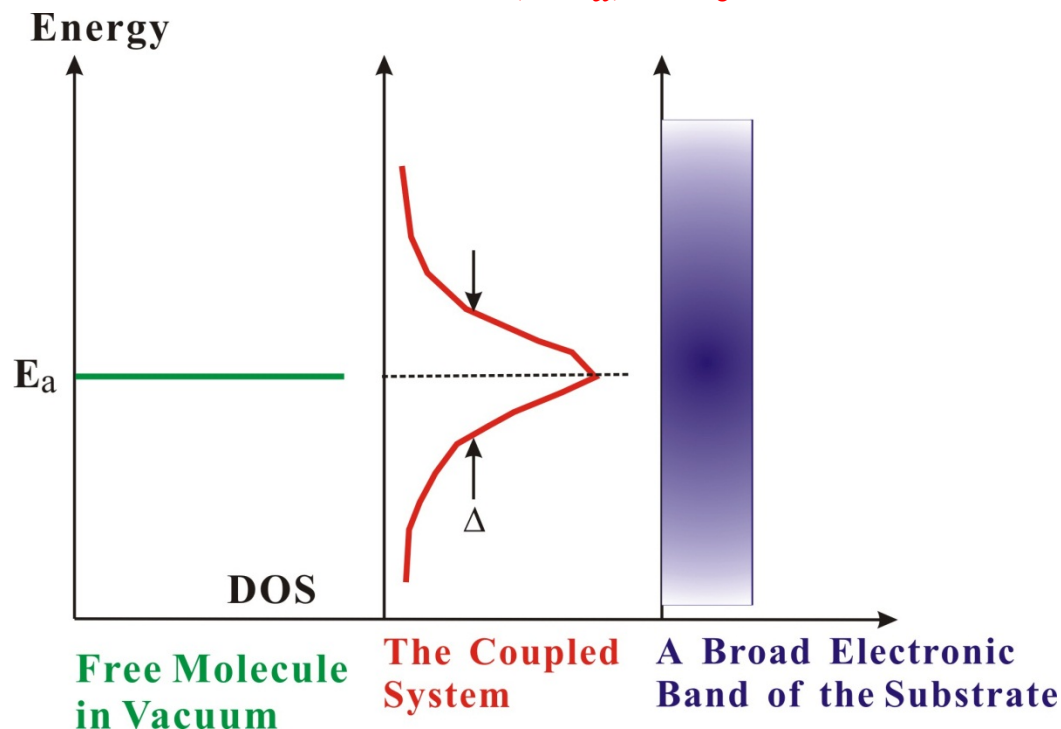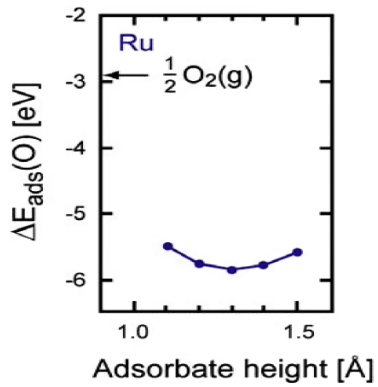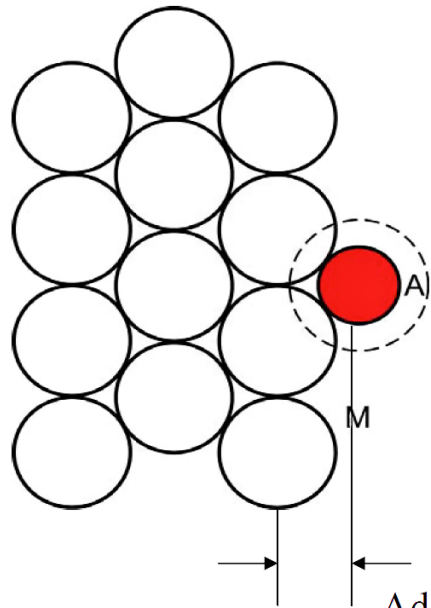**Trend:** The higher the *d*-band energy, the stronger the bonding

Theoretical Formalism of the Adsorbed System

● **Adsorbate couples to a broad *s*-band of the substrate**

If the adsorbate only couples to a broad *s*-band of the substrate,
$$\Delta(\varepsilon) = \pi|V_{as}|^2 \sum_k |< k|s >|^2 \delta(\varepsilon - \varepsilon_k) = \Delta_0 \text{ and}$$

$$\Lambda(\varepsilon) = \frac{\Delta_0}{\pi} P \int \frac{1}{\varepsilon - \varepsilon'} d\varepsilon' = 0 , \text{ resulting in}$$
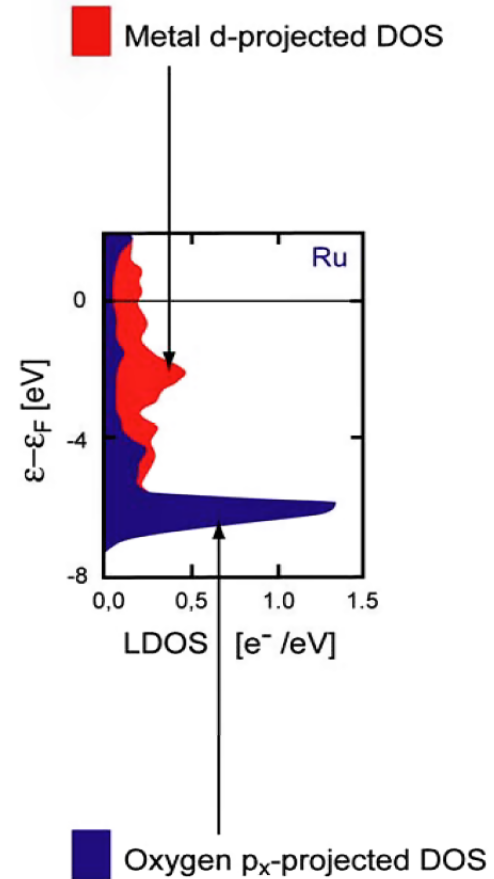
$$n_a(\varepsilon) = -\frac{1}{\pi} Im[G_{aa}] = \frac{1}{\pi} \frac{\Delta_0}{(\varepsilon - \varepsilon_a)^2 + \Delta_0^2}$$
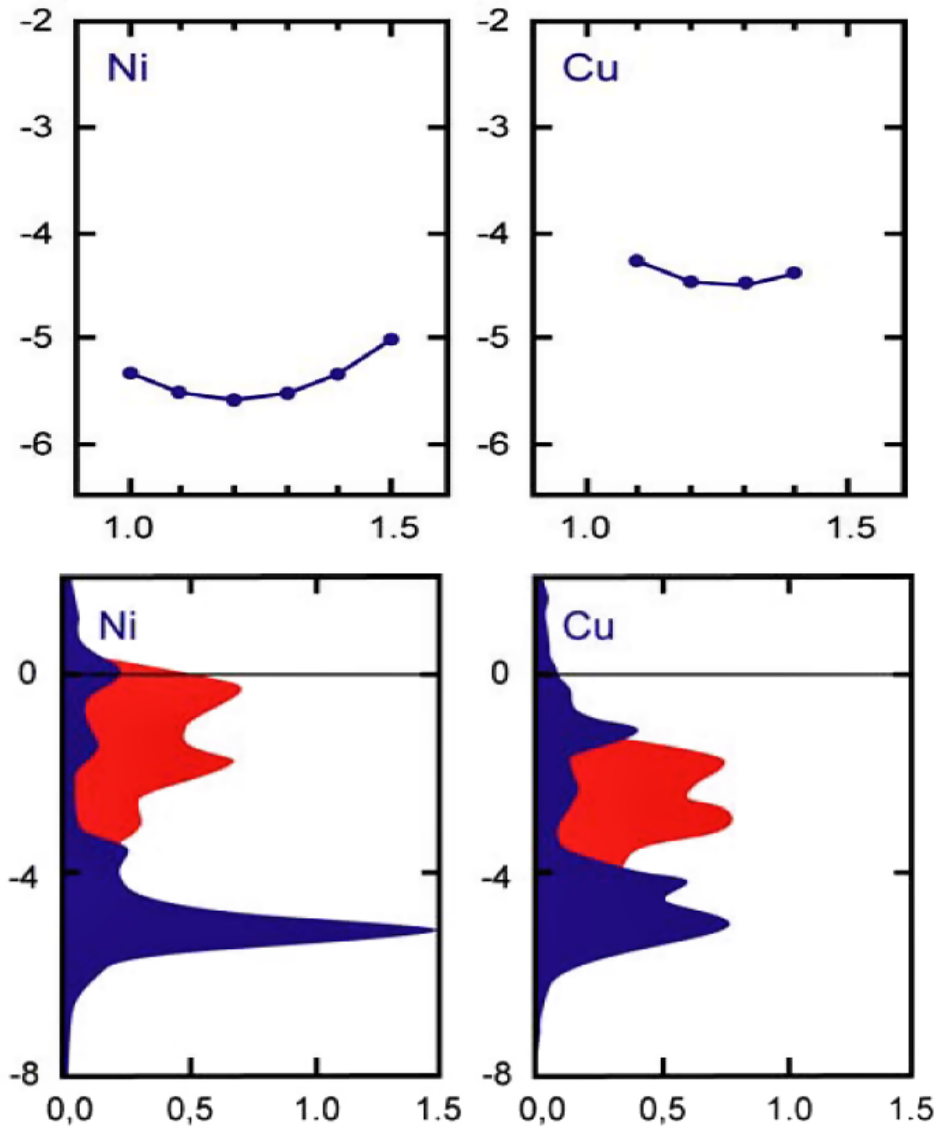

Free Molecule in Vacuum

The Coupled System

A Broad Electronic Band of the Substrate

DFT calculations O/(111) surfaces
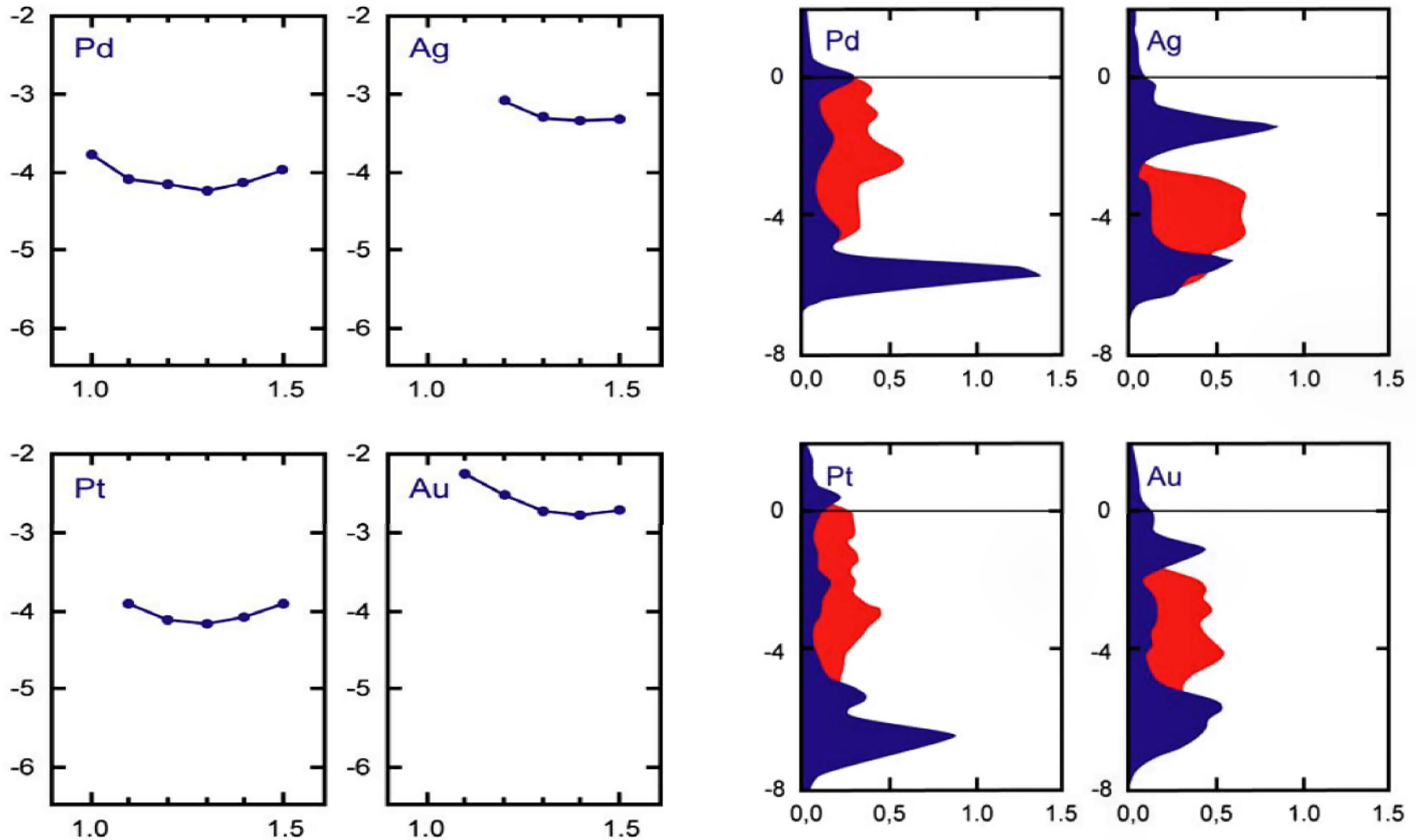

Adsorbate height
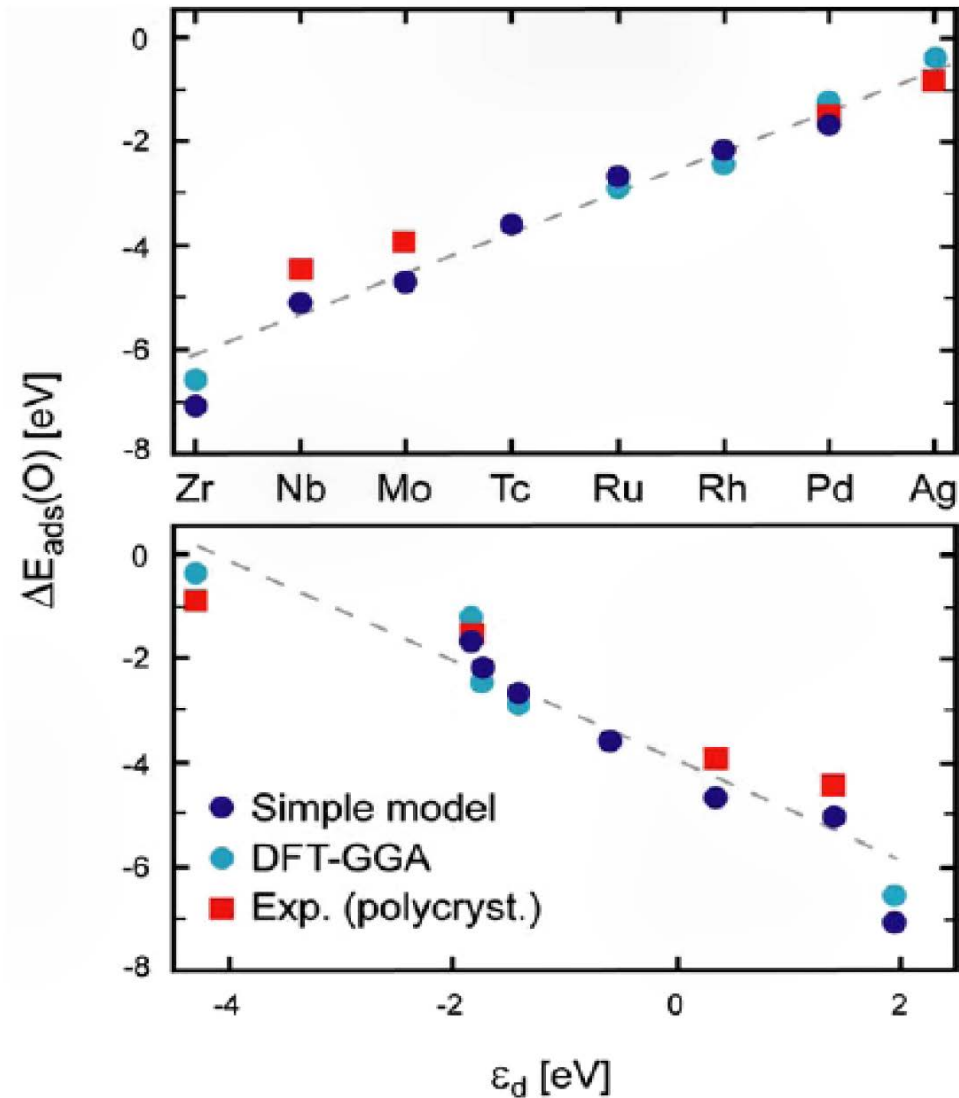above surface

DFT calculations O/(111) surfaces

DFT calculations O/(111) surfaces

Hammer, Nørskov, Adv. Catal. 45, 71 (2000)
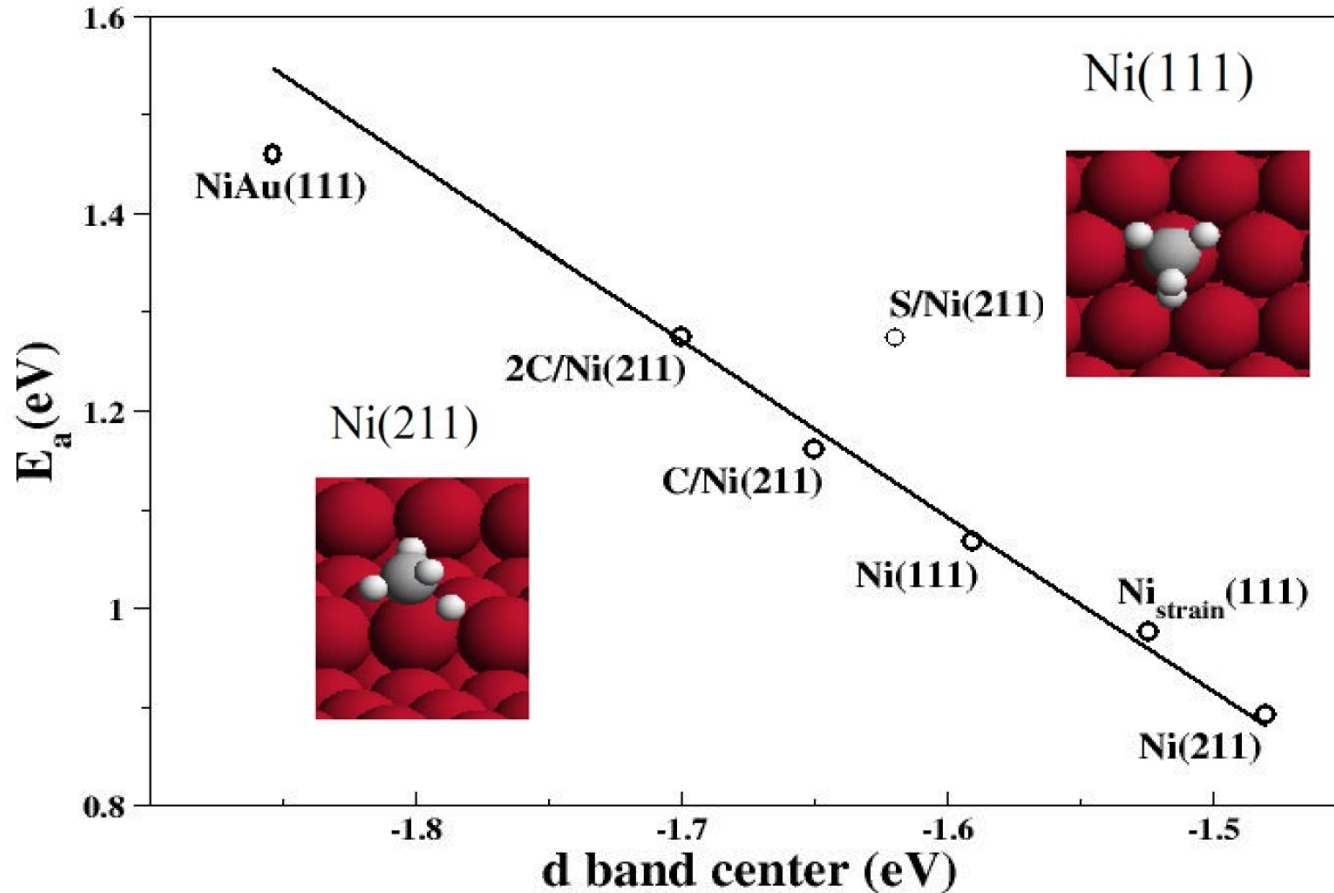
DFT calculations O/(111) surfaces
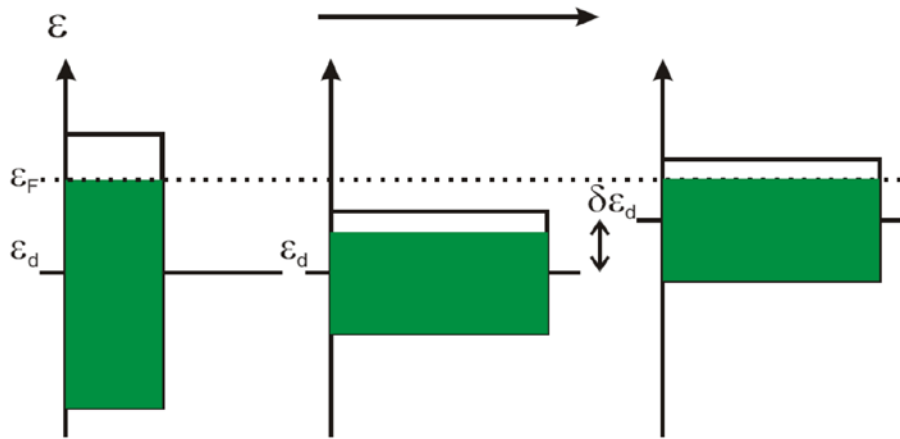
Hammer, Nørskov, Adv. Catal. 45, 71 (2000)

Exp: Toyoshima, Somorjai, Catal. Rev. Sci.Eng. 19, 105 (1979)

Similar Trends for Activation Energies E_a

Methane dissociation on Ni surfaces

Abild-Pedersen, Greeley, Nørskov, Catal. Lett. 105, 9 (2005)

Kinks, Steps, Clusters

Calculated under-coordination up-shifts (Pt)
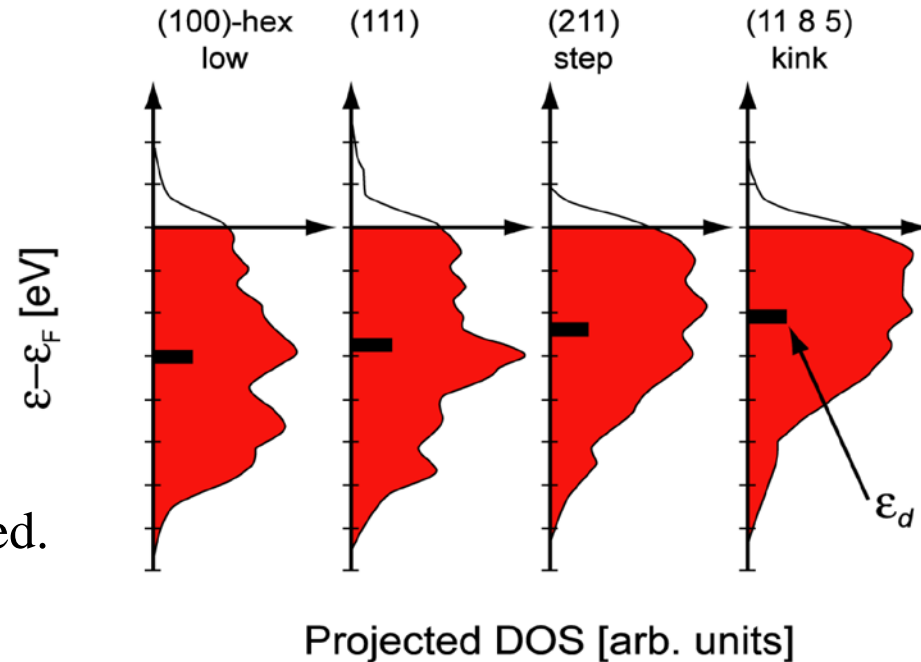
The area of DOS must be conserved due to that the total # of electrons must be conserved.

Band Width ∝ # of neighbors × hopping

When the band width is decreasing the only way of maintaining the number of d electrons is to shift up the center of the band.
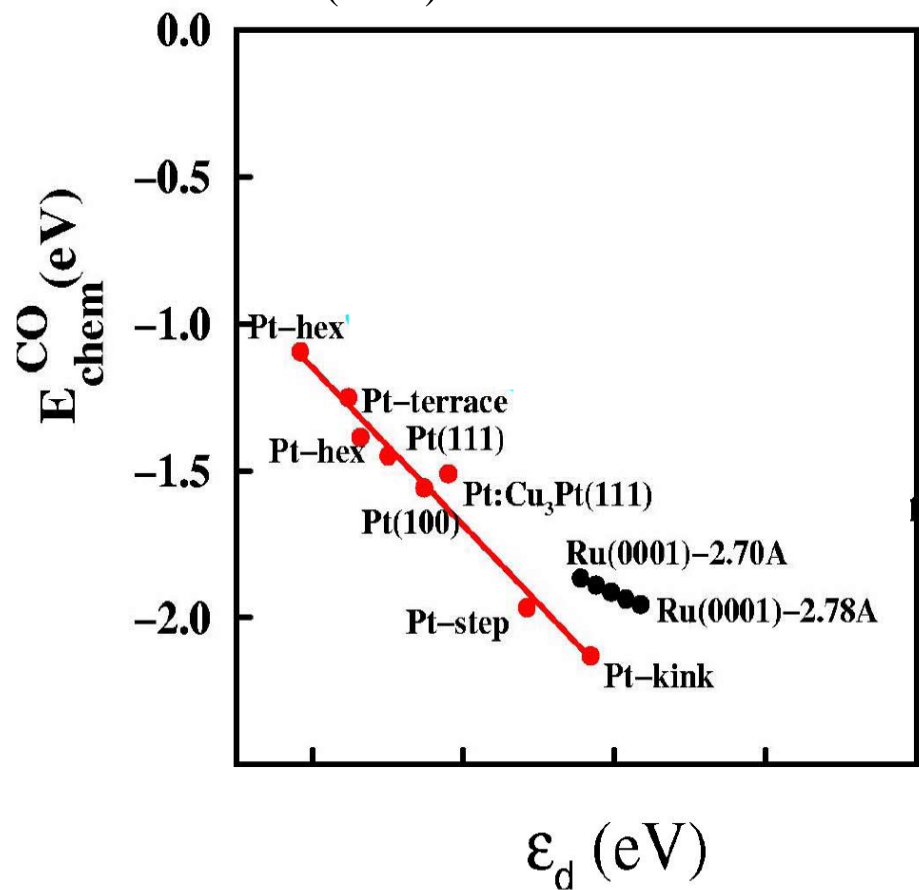
Bligaard, Nørskov, Electrochim. Acta 52, 5512-5516 (2007)

Adsorption Strength and the Surface Structures

CO chemisorption

Low-coordinated atoms bind adsorbates stronger!

Summary