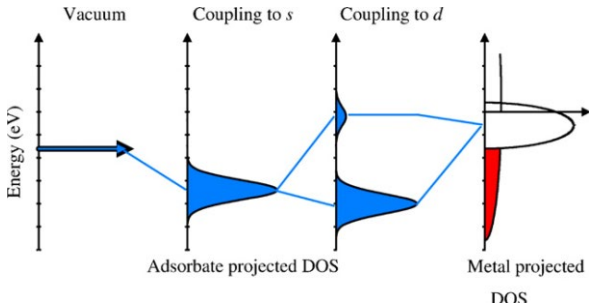
5. Computational design of catalytic materials

Contents

5.3 The d-band model

In the *d*-band model for a given reaction, variations in adsorption energies and activation barriers from one transition metal to the next are given by variations in the coupling between the levels of adsorbates and the transition metal *d*-bands. Consider an adsorbate (*a*)-metal (*m*) system in which the adsorption energy is defined as

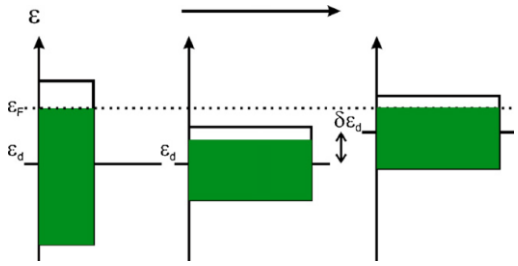
$$E_{ads}(a/m) = E(m+a) - E(m) - E(a)\,.$$



$$\Delta E = \Delta E_0 + \Delta E_d\,,$$

where ΔE_0 is the bonding energy contribution from the coupling of the adsorbate states to the free-electron-like *s*-electrons, and ΔE_d is the contribution from the extra interaction with the transition metal *d*-electrons. The model is illustrated in the Figure One of the basic assumptions of the *d*-band model is that ΔE_0 is independent of the metal. This is a reasonable first approximation since the *s*-bands of transition metals are broad and it is always half filled. However, it will fail when metal particles get small enough that the *sp* levels do not form a continuous spectrum. we can estimate the *d*-contribution as the non-self-consistent one-electron energy change as $\Delta E_d \approx \int \varepsilon\left[\Delta n'(\varepsilon) - \Delta n(\varepsilon)\right] d\varepsilon$, where $\Delta n'(\varepsilon)$ and $\Delta n(\varepsilon)$ are the adsorbate-induced

densities of states with and without the *d*-coupling included, respectively. In general, the coupling of the adsorbate states to the metal *d*-bands will depend on the energy of the adsorbate states ε_a, the projected *d*-density of states $n_d(\varepsilon)$ onto the metal atoms in direct contact to the adsorbate, and the coupling matrix element between the adsorbate and the surface states.



Schematic illustration of the coupling between bandwidth and d-band center for a band with a fixed number of *d*-electrons. When the bandwidth is decreasing the only way of maintaining the number of *d*-electrons is to shift up the center of the band.

5.4 *ab inito* Deisgn of Solid Catalysis

A goal in catalysis research is to design and tune the activity and selectivity of catalysts by controlling their structural properties at the atomic level.

A Case Study of *ab initio* Design of Solid Catalyst

Strategy of automated screening of fuel cell cathode materials for oxygen reduction reaction (ORR).

What we are looking for:

Pt alloy surfaces that bind O weaker than Pt.

What is calculated:

Material Stability (Segregation Energies)

ORR descriptors

- -O adsorption Energies
- -OH adsorption Energies
- -d-band centre position

How is this calculated:

Structure optimisation using Density Functional Theory

From calculations to materials design:

–High throughput strategies

–Data accumulation, managing and reporting