

## Theoretical aspects of heterogeneous catalysis

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# THEORETICAL ASPECTS OF HETEROGENEOUS CATALYSIS

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## Abstract

Quantum chemical aspects of chemical bonding to metal surfaces are discussed. It is demonstrated that a Frontier Orbital Theory of chemisorption can be developed in which the group orbital local density of states at the Fermi level replaces the HOMO and LUMO interactions familiar in organic or organometallic chemistry. This appears to be a useful tool to describe elementary reactions at metal surfaces. Dissociation of the  $H_2$  molecule and hydrogen atom recombination is analysed in detail. Symmetry considerations can be applied. It is shown that the interaction with antisymmetric group orbitals lowers the activation energies. Such orbitals are also available at s-valence electron metal surfaces as long as the molecule interacts in bridging coordination sites.

One finds that the interaction with metal d-valence electrons stabilizes coordination in the atop position. The relative contribution to bonding of metal s and d-valence electrons differs significantly for the transition metals. It is not only a function of metal-electron occupation number, but also of the row in the periodic system in which the metal is placed. This information is used to explain the different hydrogenolysis behaviour of Ni and Pt.

1. Introduction

The concept of chemisorption is a key to the understanding of catalytic reactions. Catalytic events consist of elementary reactions on the catalyst surface in which chemical bonds are formed between surface atoms and an adsorbing molecule. These interactions cause rupture of chemical bonds within the adsorbing molecule and formation of new chemical bonds between the fragments.

The strength of the surface chemical bond is governed by geometric as well as electronic effects. The geometric contributions can be subdivided into a primary and secondary ensemble effect [1].

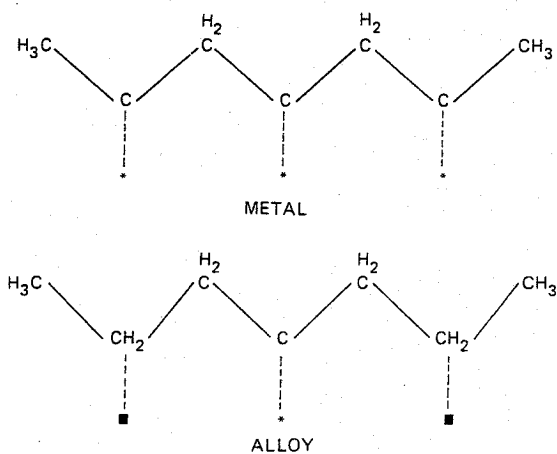


Fig. 1. Primary ensemble effect (surface topology). Alloying with an inert metal decreases the number of molecule atoms bonding to the metal surface.

According to the primary ensemble effect (Fig. 1) a molecule may adsorb to several sites on the metal surface, because the molecule binds to the surface with more than one of its atoms. Dilution of the surface by inert atoms decreases the chance of reactive neighbouring adsorption sites, which will decrease the bond strength. This concept appears to be very useful to interpret changes in hydrocarbon conversion patterns on alloy catalysts. The primary ensemble effect is determined by surface topology.

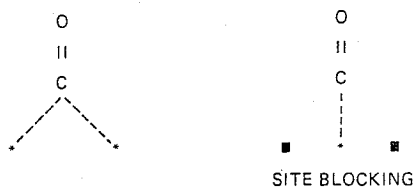


Fig. 2. Secondary ensemble effect (surface atom clusters). Alloying with an inert metal decreases the coordination number of interacting molecule atoms.

The secondary ensemble effect depends on the arrangement of surface atom neighbours. As sketched in Fig. 2 an atom by which an adsorbing molecule coordinates to the metal surface will in general bond to several surface atoms, giving an adsorbate coordination number  $Z$ . Substitution of a surface atom in the first coordination sphere of the adsorbate by another atom will change the chemisorptive bond strength, which may result in a change of coordination. As we will see, the relation between bond strength and coordination number is very sensitive to the local electron density of the ensemble of atoms involved in chemisorption.

Changes in bonding due to differences in atomic structure outside the first coordination sphere of the chemisorbed atom are interesting, because they have to be ascribed to variations in electronic structure of the surface complex formed by the chemisorbed molecule and the surface metal atoms to which it is bonded due to embedding of this surface complex in the three-dimensional surface lattice. Such changes can occur, for instance, because of alteration of the degree of coordinative unsaturation of the surface atoms, when chemisorption occurs to different faces of a material. Alloying and coadsorption may also affect chemisorption by such indirect effects. Although the changes in bond strength caused by these secondary electronic effects will be small, they are still relevant, since small relative energies are chemically important.

These secondary electronic effects may be covalent or electrostatic. Covalent electronic effects occur if bonding is changed because the local electron energy density on the atoms involved in chemisorption is varied by changes in the second coordination sphere with respect to the adsorbate. We will discuss a few examples based on Frontier Orbital Theory [2,3,4] adapted to surfaces. Emphasis will mainly be on the electron occupation and local density of states at the Fermi level.

Electrostatic effects are due to changes in the electrostatic Coulomb potential. On a lattice they give rise to the Madelung potential. At a surface the relevance of direct, long-range electrostatic effects on the chemisorptive bond has been extensively discussed for the co-adsorption of potassium with carbon monoxide on

transition-metal surfaces [5-9]. These effects can be ascribed to changes in the ionization potential and electron affinity of adsorbed molecules with respect to the Fermi level. The work function of a metal surface changes with crystal face due to differences in the surface dipole [10,11]. As a result, the ionization potential and electron affinity of adsorbed molecules will also change with respect to the bulk Fermi level. So a change in crystal face will not only affect the bond strength because of changes in adsorption topology and covalent bond strength, but also owing to changed electrostatic effects.

We will discuss the issue of the relative contribution of s and d metal valence electrons to chemisorption using experimentally observed trends in chemisorption. Also, the concepts of promotion energy and localization energy will be introduced.

Further, Frontier Orbital Theory will be applied to discuss the secondary ensemble effect and how the relative energetics are affected by secondary electronic effects.

Subsequently, we will discuss dissociative and associative adsorption of hydrogen. This models elementary steps in catalysis. Although this subject has been explored rather sparingly, elementary symmetry considerations can be very useful to understand the basic principles involved.

A new hypothesis is proposed to explain hydrogenolysis patterns observed in transition metal catalysis. In this connection the importance of the relative contributions of s- and d-valence electrons to chemisorption are seen to be crucial to understand catalytic selectivity.

In a last section we will briefly discuss electron correlation aspects of chemisorption.

## 2. Trends in chemisorption

There exists a well-known correlation between surface and bulk bond strength [12], which suggests that chemisorption and chemical bonding in solids are closely related. In general, it is found that the heat of adsorption is larger than the heat of formation of the corresponding compound. Somorjai [13] has demonstrated that the chemisorption bond strength is a strong function of the surface complex geometry, i.e. the secondary ensemble effect. March [14] and Flores e.a. [15] have developed formulae for the chemisorptive bond analogous to Pauling's [16] bond strength formulae:

$$E_{MA} = 3 \left\{ \frac{1}{2} [E(M-M) + E(A-A)] + (X_M - X_A)^2 - \left(1 - \frac{V}{12}\right) E(M-M) \right\} \quad (2.1a)$$

or

$$E_{MA} = \frac{v}{12} \left\{ \frac{1}{2} [E(M-M) + E(A-A)] + (X_M - X_A)^2 \right\} \quad (2.1b)$$

The formulae apply to dissociative adsorption, coordination number  $Z = 3$  and a (111)-face of an f.c.c. crystal.  $E(M-M)$  and  $E(A-A)$  are the bond strengths of the diatomic molecules of metal and adsorbing atoms and  $X_M$  and  $X_A$  their respective chemical affinities.  $v$  is the metal atomic valency. Since  $v < 12$ , according to both formulae the chemisorption bond strength is smaller than that of the corresponding free molecules. This is generally true, but exceptions are found. It is revealing to understand the physical basis of formulae (2.1a) and (2.1b). Formula (2.1a) is valid in the "surface molecule limit", formula (2.1b) is proposed for weak chemisorption.

Fig. 3 illustrates the three steps of which the chemisorptive bond strength for an atom coordinated to one surface atom can be considered to consist:

$$E = E_{MA} + E_{subl} + E_{emb} \quad (2.2)$$

$E_{MA}$  is the bond strength of the diatomic molecule,  $E_{subl}$  is the energy required to remove a surface metal,  $E_{emb}$  is the energy generated by embedding the diatomic molecule into the vacant surface position.  $E_{subl}$  is a measure of the metal-metal bond strength,  $N$  the number of metal atom neighbours of the surface atom. In the sur-

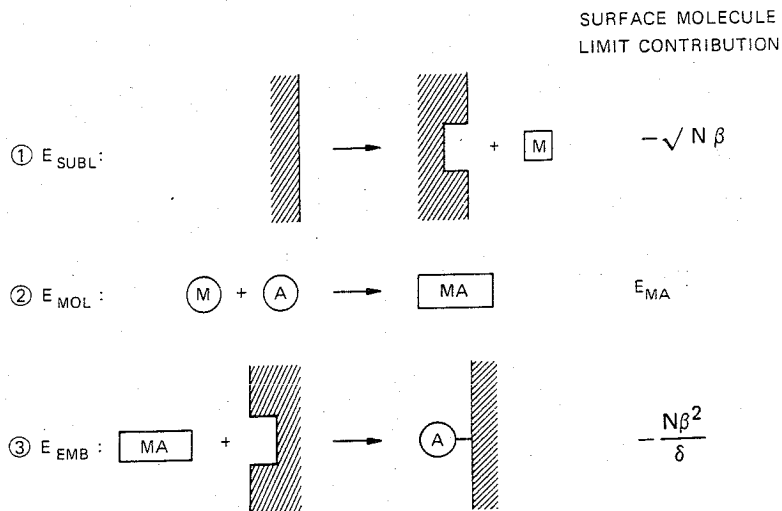


Fig. 3. Chemisorption seen as the sum of three elementary steps:  
 $E = E_{MA} + E_{subl} + E_{emb}$

face molecule limit:  $E_{\text{emb}} \ll E_{\text{subl}}$ , i.e. chemisorption is strong and  $E_{\text{emb}}$  can be estimated from second-order perturbation theory:

$$E_{\text{emb}} \approx -\sum_i \frac{N_i \beta^2}{\delta_i} \quad (2.3)$$

$\delta_i$  is the energy difference between the surface molecule levels and the Fermi level,  $N_i$  is the coordination number of the corresponding orbital. Since in the surface molecule limit  $|\beta/\delta_i| \ll 1$ ,  $\Delta E$  becomes smaller than the bond strength in the diatomic molecule, because electrons have to be localized on the atom to which chemisorption occurs. In the surface molecule limit, the bond strength to a surface is predicted to increase if the surface atoms become less saturated. This explains the generally higher heat of chemisorption compared to heat of formation.

Table 1 shows that in metal carbonyl complexes the M-H bond strengths can be larger than in the free MH molecule. In the carbonyl complex the (s) orbital is partially empty (electrons have been promoted from s to d atomic orbitals), whereas in the atom it is doubly occupied. In the case of hydrogen bonding to transition-metals of the third row of the periodic system s-orbital bonding dominates that with d-orbitals. Chemisorption of hydrogen to Cu, Pt and Au shows the expected decreases in bond strength compared to bonding in the MH molecule. It is not found for Ni; the atom again requires 4s to 3d electron promotion. Interestingly whereas the diatomic bond strength of PtH is larger than that of NiH, it inverts on the metal surface due to the secondary electronic effects. Table 1 shows that the chemisorption bond is weaker than bonding of a metal surface atom with the metal lattice.

Table 1. Comparison of metal-hydrogen bond strengths  
(kcal/mol)

M	MH <sub>mol</sub> [ref.17]	(CO <sub>4</sub> )MH [ref.18]	MH <sub>ads</sub> [ref.19]	Config. of metal atom	M-M
Mn	56	65		3d <sup>5</sup> 4s <sup>2</sup>	
Co	45	57		3d <sup>7</sup> 4s <sup>2</sup>	
Ni	60		63	3d <sup>8</sup> 4s <sup>2</sup>	17
Cu	66		56	3d <sup>10</sup> 4s <sup>1</sup>	13.7
Pt	83		57	5d <sup>9</sup> 6s <sup>1</sup>	20.3
Au	74		<52	5d <sup>10</sup> 6s <sup>1</sup>	19.6

### 3. Frontier Orbital Theory

Frontier orbital theory [3,4] enables the study of the chemical bond strength in relation to the electronic structure of the fragments before chemical bonding, and applies to weak and intermediate adsorption, the non-surface molecule limit. Fig. 4 schematically illustrates the relative electron energy distribution of an adsorbate and metal before chemisorption. The total energy can be written as a sum of two terms:

$$E = E_{\text{rep.}} + E_{\text{attr.}} \quad (3.1)$$

$E_{\text{rep.}}$  is the repulsive energy contribution that corresponds to Born repulsion originating from the penetration of the adsorbing molecule and surface electron

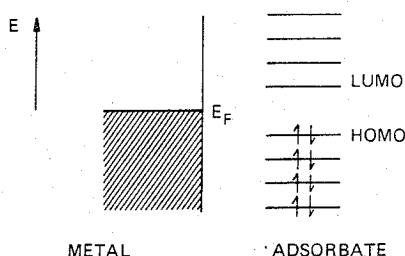


Fig. 4. Frontier Orbital Theory.  
Metal and adsorbate electron density distributions.

orbitals. As long as the electrons do not rearrange, this repulsion is proportional to the overlaps of metal and adsorbate wave functions ( $S$ ). Orthogonalization of these wave functions causes polarization of the electrons away from the bonding region, lowering the overall repulsion energy [20-22]. A rough approximation to  $E_{\text{rep.}}$  gives:

$$E_{\text{rep}} = \sqrt{Z} \cdot S \quad (3.2)$$

Frontier orbital theory assumes that orthogonalization and charge transfer occur additively.

$E_{\text{attr.}}$  is given by a second-order perturbation expression:

$$E_{\text{attr}} = -2 \left\{ \sum_{\alpha, i} |\beta'_{\alpha i}|^2 \frac{1}{\epsilon_i - \epsilon_{\alpha}} + \sum_{\beta, j} |\beta'_{\beta j}|^2 \frac{1}{\epsilon_{\beta} - \epsilon_j} \right\} \quad (3.3)$$

$$\begin{array}{ll} \epsilon_i > E_F & \epsilon_j < E_F \\ \epsilon_{\alpha} \text{ occ} & \epsilon_{\beta} \text{ unocc} \end{array}$$



$\beta'_{\alpha i}$  is the overlap energy matrix element between the Highest Occupied Molecular Orbital  $\epsilon_{\alpha}$  and unoccupied metal surface level  $\epsilon_i$ ;  $\beta'_{\beta j}$  is the overlap matrix element between the Lowest Unoccupied Molecular Orbital  $\epsilon_{\beta}$  and occupied metal surface levels  $\epsilon_j$ . Since orbitals  $\epsilon_i$  and  $\epsilon_j$  form a continuum, equation (3.3) can be partially integrated [24] to give:

$$E_{\text{attr.}} = -2 \left\{ \sum_{\alpha} \rho_{\alpha}(E_F) \beta'_{\alpha}{}^2 \frac{\Delta_{\alpha}(1 - p_{\alpha})}{E_F - \epsilon_{\alpha} + \Delta_{\alpha}(1 - p_{\alpha})} + \sum_{\beta} \rho_{\beta}(E_F) \beta'_{\beta}{}^2 \frac{\Delta_{\beta} \cdot p_{\beta}}{\epsilon_{\beta} - E_F + \Delta_{\beta} \cdot p_{\beta}} \right\} \quad (3.4)$$

$\epsilon_{\alpha} < E_F$   
 $\epsilon_{\beta} > E_F$

$\rho_{\alpha}(E_F)$  is the group orbital electron density at the metal Fermi level energy [23]:

$$\rho_{\alpha}(E_F) = \sum_i |\langle \varphi_{\alpha} | \psi_i \rangle|^2 \delta(E_F - \epsilon_i) \quad (3.5a)$$

$\varphi_{\alpha}$  is a linear combination of surface atomic orbitals,  $\psi_i$  a metal surface eigen function with corresponding energy  $\epsilon_i$ .

$$\beta'_{\alpha} = \langle \chi_{\alpha} | H' | \varphi_{\alpha} \rangle \approx Z_{\alpha}^{\frac{1}{2}} \beta'_{\alpha}(Z_{\alpha} = 1) \quad (3.5b)$$

$Z_{\alpha}$  is the number of surface metal atom neighbours.

Since  $H'$  is totally symmetric,  $\chi_{\alpha}$  (the adsorbate molecular orbital) determines the symmetry of surface complex metal orbital  $\varphi_{\alpha}$ , the group orbital. This has been discussed extensively elsewhere [6,24].

$\Delta_{\alpha}$  is the total band width of the metal valence electron band corresponding to  $\varphi_{\alpha}$ , and  $p_{\alpha}$  is a measure of the electron occupation of that electron band:

$$p_{\alpha} = \frac{E_F}{\Delta_{\alpha}} \quad (3.6)$$

Expression (3.4) contains the important result that the attractive contribution to the bond strength caused by virtual charge transfer between adsorbate and metal surface depends on four parameters:

- (a) the group orbital local density of states at the surface metal Fermi level
- (b) the energy difference between adsorbate orbitals and the surface Fermi level
- (c) the surface metal orbital electron occupation
- (d) orbital overlap.

In a recent paper J.P. Ia Femina and J.P. Lowe [25] presented related ideas using Frontier Crystal Orbitals. Also Minot [26] considered the use of surface amplitude patterns.

Figure 5 shows the LDOS of different group orbitals of the s-band for the (111)-face of a f.c.c. crystal [6]. It is observed that at an electron occupation number of one electron per atom and an adsorbate orbital of  $\sigma$  symmetry

$$\rho_{\text{atop},\sigma}(E_F) > \rho_{\text{bridge},\sigma}(E_F).$$

Interestingly, Hermann [22] concluded from a Hartree-Fock calculation of chemisorption of  $\text{NH}_3$  to Cu clusters modelling atop and bridge coordination to the Cu(111) surface, that the attractive interaction between the doubly occupied lone pair orbital of  $\sigma$  symmetry of  $\text{NH}_3$  and the metal surface favours atop coordination. Atop adsorption instead of to the Freundlich site indicates that electronic rather than topological criteria determine the relative stability of adsorbed molecules. The chemisorption of carbon monoxide to the Pt(111), Rh(111) and Cu(111) faces indicates the same [6]. On these faces the atop position is favoured. The coordination of CO can be considered to be due to an electron donation term from the metal to the unoccupied antisymmetric  $2\pi^*$  orbitals of CO and a backdonation term dominated by interaction of the symmetric  $5\sigma$  orbital and the metal surface. Since the unoccupied  $2\pi^*$  orbital does not interact with the symmetric s atomic

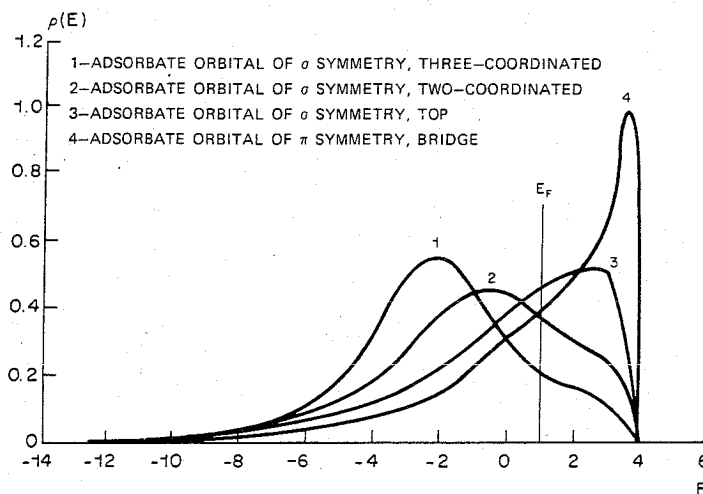


Fig. 5 Group orbital local density of states at the (111) face of the s-valence electron band of an f.c.c. metal ( $\beta = -1$ ;  $E_F = 1$  when electron density equals one electron per atom).

orbitals in the atop position, interaction with the s-band forces the molecule in the bridge position.

However as we have seen for ammonia the interaction of the  $5\sigma$  orbital directs the molecule in the atop position. This holds for the interaction with the s-band as well as the highly filled d-band [5]. It appears therefore that a low work function favours bridge coordination, but strong interaction with the highly filled d-band favours atop coordination. If bonding becomes weak, as in the case of Cu, Born repulsion terms may become significant again, favouring coordination in the atop position [24,27].

LAPW calculations by Wimmer e.a. [28] show that alkali ions adsorbed to the metal surface lower the relative energies of the CO  $2\pi^*$  and  $5\sigma$  levels with respect to the metal surface Fermi level. So the interaction with electron accepting  $2\pi^*$  levels is enhanced and that with the electron donating  $5\sigma$  levels decreases, explaining the shift from top to bridge position and the increase in bond strength of CO chemisorbed to the Pt(111) face doped with potassium ions [5]. Because electrons are accumulated on the surface atoms next to the alkali ion to screen its charge, the local density of states at the Fermi level also changes. We have shown that this also tends to favour bridge coordination. The energetic effect of the change in LDOS, however, is a decrease in the adsorbate bond strength, since now the decrease in the interaction with the  $5\sigma$  level is not compensated for by the enhanced interaction with the  $2\pi^*$  level [5]. The observed increase in CO bond strength proves that the direct electrostatic interaction between potassium ion and adsorbed CO dominates.

Fig. 6 shows the hydrogen bond strength for hydrogen adsorbed to the (111)-face of a f.c.c. crystal as a function of electron occupation and degree of surface unsaturation. It is seen that at low electron occupation a high coordination number of the metal surface atoms decreases the bond strength, but we find a different situation at high electron occupation. The behaviour at low electron density agrees with what one would expect on the basis of changes in electron localization energy. More surface atom neighbours increase the electron localization energy, which decreases the bond strength. The change at high electron occupation can be understood when we study local density of states of the surface atom at the Fermi level. More surface atom neighbours increase the width of the local electron density. As a result, at the edges of the band the electron density increases, but at the centre of the band the electron density will decrease [6]. Since the local electron density width at the surface is smaller than in the bulk, one expects for the group VIII metals an increase in d-electron band occupation at the surface [29]. On this basis Tersoff and Falicow [30] predict that bonding with an adatom

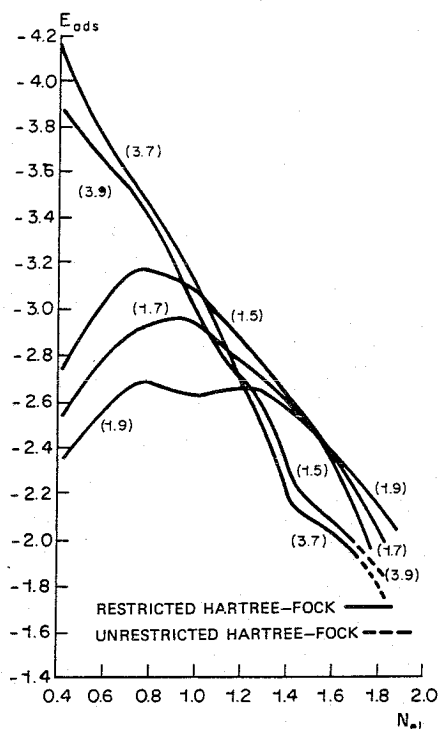


Fig. 6 Interaction energy  $E_{ads}$  of a hydrogen atom to the (111)-face of an s-valence electron band of a f.c.c. crystal as a function of  $N_{el}$ .

Numbers in brackets:  $(Z_C, Z_S)$ ,

$Z_C$  : adatom coordination number

$Z_S$  : surface metal atom metal  
neighbour atoms.

$N_{el}$  : number of electrons per metal atom in bulk metal.

increases if bonding occurs to a subsurface group VIII atom of high coordination number. Fig. 6 shows that indeed the bond strength may increase if this is accompanied by a decrease in electron occupation, but that the effects due to changes in the band width tend to dominate, counteracting the electron occupation decrease effects. Only at very high band occupation would this also result in an increase in bond strength. We have argued elsewhere [6] that in group VIII metals the valence-electron occupation is such that this very high band occupation situation does not occur.

#### 4. Surface reactions

A major advance in the theory of reactivity has been the development of the Woodward-Hoffmann rules [31] which relate the activation energy of a reaction to the symmetry of the orbitals of the reactants involved. Pearson [32] formulated that the symmetries of the Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) have to be the same in order that a reaction proceeds. The validity of this rule has been demonstrated in numerous examples. These rules can be applied to chemisorption and surface reactions if one takes the group orbital local density of state at the Fermi level to represent the interacting HOMO and LUMO coefficients of the metal surface.

We will illustrate this for hydrogen dissociation to a string of Cu atoms, represented by 1 s orbital per atom with an electron occupation of one electron per atom. Although the interaction of H<sub>2</sub> with a Cu atom has not been studied, it has been found that CH<sub>4</sub> only dissociates upon reaction with Cu, if the Cu s-electron becomes excited to a p-orbital [33]. No dissociation in the ground state occurs because the HOMO and LUMO of the Cu atom and CH<sub>4</sub> molecule, respectively, do not match. The antisymmetric 4p Cu orbital, however, matches in symmetry with a LUMO of CH<sub>4</sub>.

The reaction of H<sub>2</sub> with Cu<sub>2</sub>, too, is symmetry forbidden, because in the parallel configuration the HOMOs and LUMOs have different symmetries and the occupied orbitals have the same symmetry, leading to Born repulsion. (The activation-energy will be small, because the Cu-Cu interaction is small compared to the H-H and Cu-H interactions.). This changes if the Cu<sub>2</sub> molecule becomes embedded in the Cu surface lattice. As we saw earlier for the f.c.c. face, a group orbital with anti-symmetric coefficients on neighbouring Cu atoms gets a finite probability to be partially occupied at the Fermi level. For a chain of Cu atoms one finds a symmetric energy density distribution for the antibonding and bonding group orbitals (Fig. 7). The electron density of the  $\sigma$  and  $\sigma^*$  orbitals of H<sub>2</sub> with increasing interaction with Cu is schematically shown in Figs. 8a and 8b. As the  $\sigma$  as well as  $\sigma^*$  orbital interacts with the Cu-chain the electron density of both orbitals broadens and they will start to overlap. If the H<sub>2</sub> distance decreases, the difference between the  $\sigma$  and  $\sigma^*$  M.O energies decreases, which enhances the overlap further. As a result, electrons will be removed from the  $\sigma$  orbital and the  $\sigma^*$  orbital will become occupied. This weakens the H<sub>2</sub> bond strength, favouring dissociation.

The activation energy for H<sub>2</sub> dissociation decreases for two reasons:

- (1) the hydrogen-hydrogen interaction is replaced by a metal hydrogen interaction,
- (2) weakening of the H-H interaction by population of the H<sub>2</sub> antibonding  $\sigma^*$  orbital and depopulation of the H<sub>2</sub>  $\sigma$  orbital.

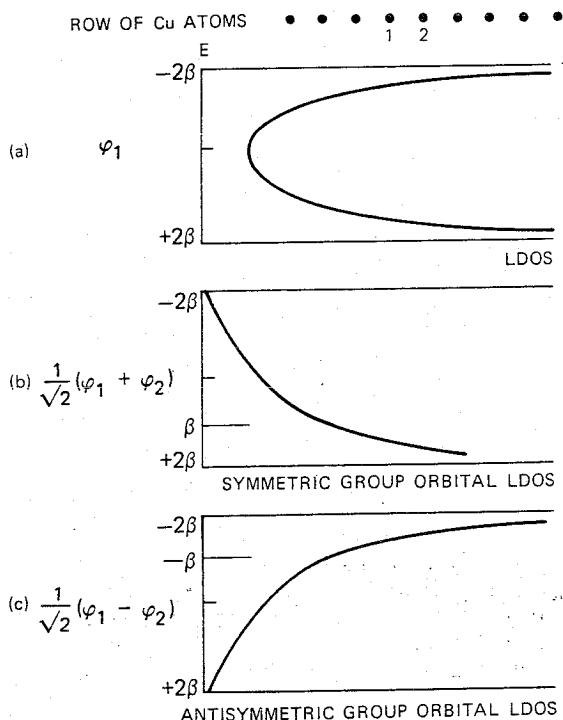


Fig. 7 a. Local density of states at an atom of an infinite string of s-orbitals.  
 b. Group orbital local density of states of symmetric group orbital:  
 $\frac{1}{\sqrt{2}} (\varphi_1 + \varphi_2)$   
 c. Group orbital local density of states of asymmetric group orbital:  
 $\frac{1}{\sqrt{2}} (\varphi_1 - \varphi_2)$

Extended Hückel calculations by R.C. Baetzold [34], Saillard and Hoffman [35], confirm the generality of this picture for the interaction of  $H_2$  with transition metal surfaces. P. Madhavan and J.C. Whitten [36], using ab initio CI calculations, find that, although the H atom favours adsorption in the atop or bridging position of the Cu(100) face and has an equal interaction energy in both configurations, the  $H_2$  molecule favours strongly the bridge and fourfold positions, where antibonding  $\sigma^*$  orbitals of  $H_2$  become populated.

Fig. 8b illustrates association, starting with hydrogen atoms adsorbed to Cu. The CuH bond has a strength of close to half the dissociation energy of hydrogen, much larger than the Cu-Cu dissociation energy. As a result, the electron distribution of CuH shows a sharp peak a few eV below the Fermi level, corresponding

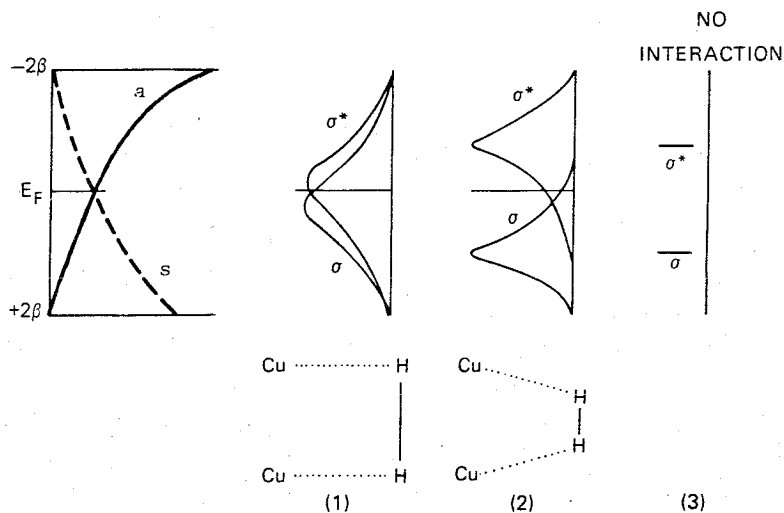


Fig. 8a Interaction of  $H_2$  with string of s-electron orbitals parallel to string. Changes in local density of states.

- (1)  $H_2$  strongly interacting with atom string: H-H distance stretched
- (2)  $H_2$  weakly interacting with atom string: no change in H-H distance
- (3)  $H_2$  at infinite distance

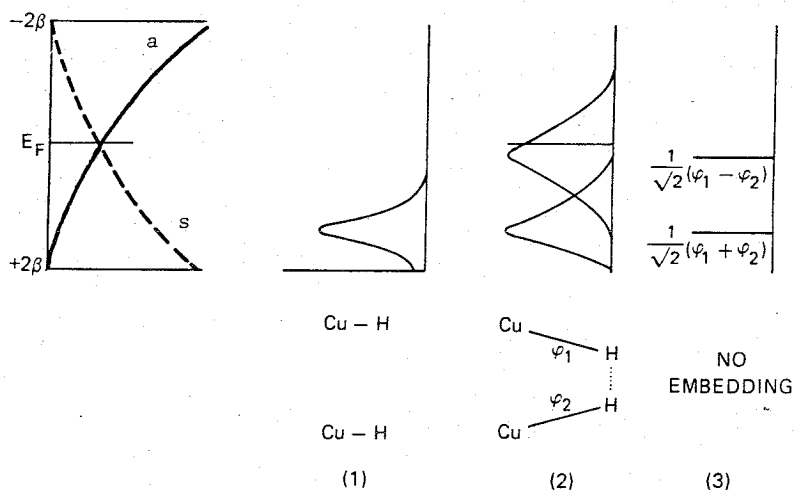


Fig. 8b Reductive elimination of  $H_2$ . Changes in local densities of states.

- (1) Isolated hydrogen atoms adsorbed to the string of s-electron orbitals
- (2) Interacting hydrogen atoms adsorbed to the s-electron string
- (3) Interacting CuH molecules without interaction with the Cu atom string

with a doubly occupied bonding CuH orbital. If two such CuH orbitals interact, for instance on two neighbouring Cu atoms, a bonding orbital of  $\sigma$  and an antibonding orbital of  $\sigma^*$  symmetry will be formed. If the interaction with the Cu lattice is ignored, both will be doubly occupied, leading to repulsion. Since both orbitals have a finite overlap with the Cu surface lattice eigen function, the  $\sigma$  as well as the  $\sigma^*$  orbital density of states will broaden. As a result, some of the density of the  $\sigma^*$  orbital will become higher than the Fermi level, and charge will flow from Cu-H to the Cu lattice. We are dealing with the analogue of reductive elimination well known in homogeneous catalysis\* [37,38]. Depopulation of the  $\sigma^*$  level reduces the hydrogen-hydrogen repulsion energy so that the atoms are allowed to approach, finally giving hydrogen association.

The molecular orbitals of the four-atom H-Cu-Cu-H complex are sketched in Fig. 9a, for the fictitious situation that all overlap energy integrals are identical. Since the H coefficients in the highest occupied orbital in this complex have the reverse sign, ring closure is Woodward-Hoffmann forbidden, so that hydrogen recombination cannot occur. If the complex becomes embedded in the metal lattice states with inversion of sign of the overlap energy integral between the Cu-H atoms become possible (Fig. 9b). This Möbius ring has a highest occupied molecular orbital with coefficients of the same sign, which implies that ring closure is now Woodward-Hoffmann allowed. If the hydrogen molecule is adsorbed atop of Cu parallel to the surface, no interaction between the  $\sigma^*$  level and the Cu-4s orbital is possible, hence the perpendicular configuration becomes favoured. This is also found for the atop position of Ni [34,35], the interaction with the d-valence electron band being small. In the bridged coordination site parallel adsorption is favoured because of the interaction with the  $\sigma^*$  level, leading to dissociation.

In metals with large d-orbitals this may change, because d-orbitals become occupied with a symmetry such that H<sub>2</sub>  $\sigma^*$  orbitals parallel to the surface in the atop configuration may interact, and reductive elimination by combination of two hydrogen atoms coordinated to a single metal atom may occur because the  $\sigma^*$  interacts with unoccupied d-electrons as has been proposed for organo-metallic complexes [37,38].

No calculations on dissociative adsorption have been published for Pt. The interaction with the d-band is expected to be stronger for Pt than for Ni, because of the much broader d-band of Pt. The increased bond strength of CO coordinated to Pt when compared to Ni indicates this as well [27]. So atop dissociation on a Pt surface may be more favoured than on a Ni surface. This would explain an interesting catalytic effect, which has so far not been well understood.

It appears that hydrogenolysis of alkanes proceeds very differently if catalysed by Pt instead of Ni. On Ni mainly methane is formed, whereas on Pt a more uniform



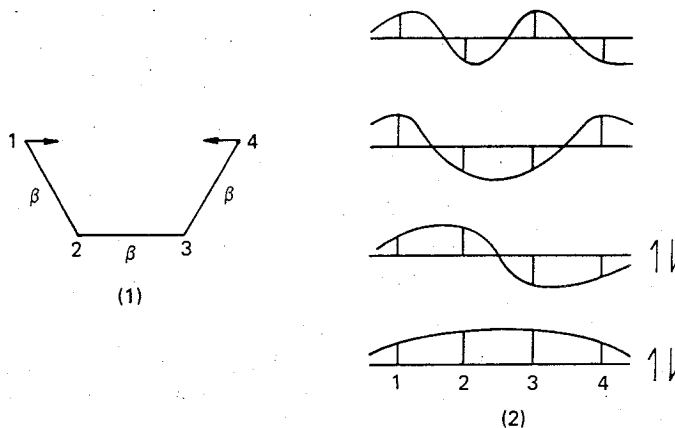


Fig. 9a Woodward-Hoffmann ring closure rules:

- (1) the H-Cu-H complex
- (2) the coefficients of the molecular orbitals of the H-Cu-Cu-H complex using a minimal s-atomic orbital basis and equal elements.

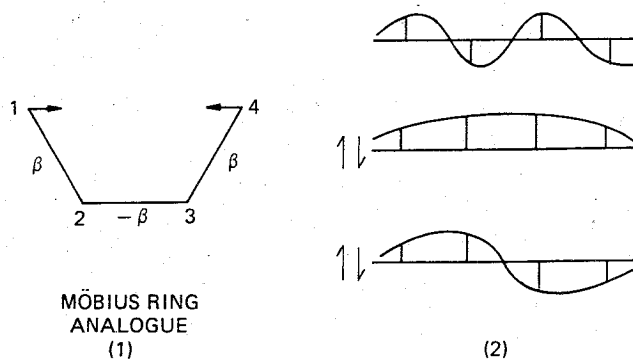


Fig. 9b Woodward-Hoffmann ring closure rules:

Inversion of the sign of Cu-Cu overlap energy integral.

- (1) the H-Cu-Cu-H complex
- (2) the coefficients of the lowest three molecular orbitals of the H-Cu-Cu-H complex.

cracking pattern is found [39,40]. Alloying of Ni with Cu makes its behaviour more Pt-like [40]. Methane production implies domination of carbon-carbon dissociation between primary and secondary atoms. Minot et al. [41] have made an interesting analysis of the coordination of alkyl groups to a transition metal surface. They found that hybridization of the carbon atom attached to the metal surface significantly affects the coordination of the hydrocarbon fragment to the metal surface. A primary C-atom prefers coordination to three metal atoms, after losing its 3 hydrogen atoms. Secondary and tertiary C-atoms prefer bridge or atop coordination. Since the interaction with the d-electrons of Ni is much less than that with Pt [27], with Ni the interaction with the s-valence electrons dominates. A strong preference for bridge of threefold coordination will be found for Ni. On the other hand, Pt will also tend to favour atop coordination.

It is well documented [42,43] that alkane activation occurs by CH dissociation followed by C-C splitting. Coordination of primary C-atoms tends to be favoured on Ni in three coordination, whereas secondary C atoms and tertiary C atoms become also activated on Pt. Upon alloying with inert metal atoms according to the secondary ensemble effect atop coordination becomes favoured, suppressing activation of primary carbon atoms on Ni, hence making it behave more like Pt. This explains the Pt type behaviour of Ni alloyed with Cu in hydrogenolysis reactions.

The particle size effect observed in the hydrogenolysis of methylcyclopentane catalysed by Pt may have a related explanation, again due to subtle changes in electronic structure [44].

Hydrogen-type adsorption to a metal becomes more favoured in bridging or higher coordination sites, if one compares small particles with large particles [27]. s-Type orbitals interact only with totally symmetric combinations of surface orbitals. In a small particle these are orbitals of low energies and they will have little weight in the HOMOs or LUMOs of the metal particle. Hence, unless the particle has a very low electron occupation (as in an ion), and the interaction between adatom and particle is weak, atop coordination will be favoured. At a surface totally symmetric group orbitals will have a finite density at the Fermi levels, as is demonstrated in Fig. 5. As discussed earlier, if electron occupation is high, again the atop position becomes favoured. However, the interaction with group orbitals corresponding to bridge or higher coordination is strongly enhanced compared to that in the smaller particles.

Methylcyclopentane ring opening occurs preferentially between the secondary carbon atoms on large Pt particles. However, with small particles non-selective ring opening, involving the tertiary carbon atoms, producing hexane is also possible.

A Pt surface favours atop coordination with respect to Ni because the highly occupied d-band enhances atop directing interactions. This atop directing effect is

even stronger for small Pt particles, because s-band effects become also stronger atop directing. Attachment to a tertiary carbon atom, required for non-selective methylcyclopentane ring opening, is strongest to the atop position, according to the Minot, Van Hove and Somorjai [41] hybridization principle. This clearly is optimum for small Pt particles, which may explain their unique catalysis.

Finally, a comment has to be made on the very strong interactions observed for particles with a size of 3 or 4 atoms [45,46]. In such particles antibonding levels of low ionization potential become occupied, which have a symmetry suitable for dissociation reactions or backdonation. This causes enhanced bridge or multi-coordination of CO on small particles [21]. If the size of the particles increases, the affinity of those levels decreases because of increased electron delocalization. Calculations by Minot et al. [47] illustrate this behaviour.

### 5. Electron correlation effects

Electron correlation will not only affect the bond strength of molecules adsorbed to the metal surface, but also influences bonding within the molecule itself. Electron correlation effects can best be understood using a Valence Bond [48] representation of the chemical bond. We will first discuss this for a hydrogen atom type adsorbate and later also consider chemisorption of the hydrogen molecule. Fig. 10 illustrates the change in local density of states of the adsorbate one electron level when it interacts with the metal surface. The width of the Lorentzian electron energy distribution  $2\Gamma$  is proportional to the electron tunneling rate  $r$ :

$$r = \frac{2\Gamma}{\hbar} = \tau^{-1} \quad (5.1)$$

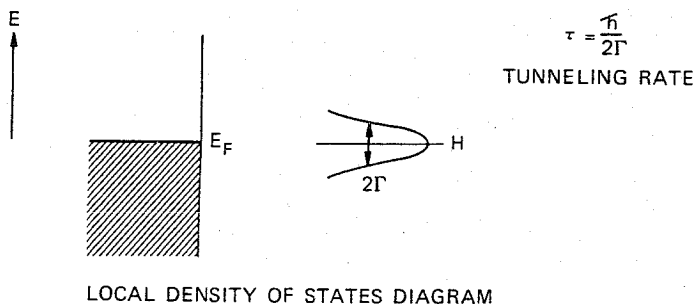
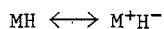


Fig. 10 Local density of states diagram for an hydrogen atom weakly interacting with a metal surface.

At infinite distance this rate goes to zero. Bonding of the adatom with the metal surface can be described in a Valence Bond representation [49] as a resonance between states as:



The energy change depends on the effective repulsive integral  $U_{\text{eff}}$  that two electrons on the adatom experience modified by electrostatic terms generated in the metal. We have shown elsewhere [50] that  $U_{\text{eff}}$  is a function of the electron tunneling time  $\tau$ :

$$U_{\text{eff}}(\tau) = U_{\text{eff}}(\tau = \infty) - \frac{1}{2z} \frac{\frac{1}{2} \omega_p^2 \tau^2}{1 + \frac{1}{2} \omega_p^2 \tau^2} \quad (5.2)$$

$$\lim_{\tau \rightarrow \infty}$$

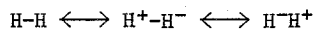
$z$  being the adatom surface distance.

The negative charge on the adatom is screened by the image potential as long as:

$$\tau^{-1} \ll \frac{1}{\sqrt{2}} \omega_p \quad (5.3)$$

$\omega_p$  is the metal plasmon frequency. Expression (5.2) implies that the metal electron motion is much faster than the tunneling rate of the adatom. March and co-workers [51] have found that a  $H_2$  molecule adsorbed parallel or perpendicular to the metal surface is stabilized differently by this image potential effect. This can be explained if one considers the ionic states of the  $H_2$  molecule as illustrated in Fig. 11.

Chemical bonding in  $H_2$  can be considered a resonance of states:

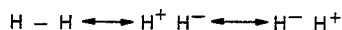


The ionic states are stabilized by the induced image potential as long as:

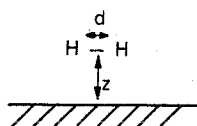
$$\frac{1}{\sqrt{2}} \omega_p \gg \omega_{\text{exc}}(H_2)$$

Then the oscillation frequency of the charge fluctuations in the hydrogen molecule ( $\omega_{\text{exc}}(H_2)$ ) is much lower than that in the metal. One calculates readily that ionic states perpendicular to the metal surface are more stabilized by the induced image potential than parallel to the surface (see Fig. 11).

As long as bonding to the surface is weak and charge fluctuations between metal

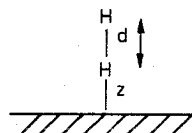


IONIC STATES ARE STABILIZED BY IMAGE POTENTIAL



$$-\frac{d}{8z^2} \left( \frac{d}{4z} \right)$$

IMAGE POTENTIAL CONTRIBUTION



$$-\frac{d}{8z^2}$$

IMAGE POTENTIAL CONTRIBUTION

$$z \gg d$$

$$\omega_p \gg \omega_{\text{exc}}(\text{H}_2)$$

Fig. 11 Resonance theory.

surface and admolecule do not dominate bonding (which give rise to chemisorption) image potential effects may influence the geometry of adsorbed molecules.

### 6. Conclusions

Theoretical studies of heterogeneous catalysis aim to provide a conceptual framework that will help the catalytic chemist to select conditions under which desired reactions occur on a catalyst surface. We have here demonstrated the importance of changes in surface electronic structure to the selectivity of surface reactions on the basis of elementary solid state quantum chemical considerations. This is a significant advance in heterogeneous catalysis, which has long rejected the relevance of the classical electronic factor on the basis of studies in alloy catalysis [1] which demonstrated the inadequacy of relating the bulk Fermi level electron density to surface phenomena. Here we show that changes in the surface group orbital local density of states at the Fermi level are relevant to changes of the chemisorptive bond. Secondary electronic effects may be insignificant, as in Pt/Au alloys [52] or significant as is observed for S coadsorption [53,54]. In Pt/Au alloys changes in s/p valence local electron density of states on Pt are small, some change occurs for the d-valence electrons. Large changes in the local density of states of the s/p valence electron band have been calculated in the case of S adsorption [55]. Chemisorption will be affected dependent on the rela-

tive contributions of s and d-valence electrons to the chemisorptive bond, as we extensively discussed earlier [6,27].

Whereas for a long time catalysis has been considered an art rather than a science, at present advances in experimentation as well as computational chemistry are rapidly extending the scientific basis of heterogeneous catalysis. We have indicated, that for simple model systems considerations analogous to molecular orbital theory used extensively in organic chemistry and homogeneous catalysis can be used to estimate the structure of adsorbate intermediates or to guess a surface reaction path. The important change is to think in terms of local energy densities, instead of the formation of discrete bonding and antibonding orbitals.

Koutecky [56,57] has made important contributions to the computation of surface states, which have led to useful techniques currently used to calculate electron densities in semi-empirical adsorption calculations. It is a pleasure to dedicate this paper to him and his work.

\*Note added in proof: R. Hoffmann recently [58] presented a related discussion of methyl fragment recombination on third row transition-metal surfaces.

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