Reactivity of transition-metal surfaces

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Rules of chemisorption of atoms and molecules to transition-metal surfaces are analyzed in terms of the distribution of electrons over bonding and antibonding adsorbate–surface orbital fragments. The larger reactivity of low index planes compared to that of the higher index planes is shown to be related to the lower localization energies of valence electrons when the coordination number of surface atoms decreases. For molecular adsorption the relative stability of adsorption complexes is controlled by the balance of donating and backdonating interaction terms.

Keywords: Chemisorption; quantum chemistry; surface electronic structure; coordination; group orbitals

1. Introduction

Experimental [1–3] as well as theoretical progress [4–7] has elucidated the nature of the surface chemical bond considerably. Surface science studies of well-defined systems have provided us with knowledge of the surface structures and relative stabilities of the chemisorbed layers. Particle beam studies are providing information on the reactivity of metal particles as a function of particle size [8]. Computational techniques are reaching a level of sophistication, where chemically relevant models can be studied [9]. In this paper we will summarize the rules of chemisorption that emerge and discuss their electronic basis.

A significant question is how properties of the chemisorbed state relate to that of the undisturbed surface. Another of especial interest to catalysis concerns the energetics of dissociative adsorption; a reaction step that is often rate-limiting in the catalytic reaction cycle.

A classical discussion in catalysis concerns the importance of the "electronic" factor versus the "geometric" one. It has indeed become clear, that often structural effects are of primary importance [10]. However, the energetic changes that are their consequence are due to electronic changes in the nature of the surface chemical bond. For a chemical approach to surface reactivity an analysis of the chemisorption complex in terms of the number and kinds of atoms present in the first and second coordination shell with respect to the adsorbate is essential.

When a molecule or atom adsorbs to surface atoms, there is a local rearrangement of electrons and change in atom positions. The local nature of the interaction does not necessarily imply that chemisorption or adsorption is a weak interaction. Whereas a typical value for the bond strength of a metal–metal bond is 80 kJ/mol, for the interaction with adatoms typical values are 700 kJ/mol. Chemisorption usually causes a weakening of the metal–metal bonds next to the chemisorbed molecule or atom. This effect is the most significant when the interaction with the adsorbate increases. Any theory of chemisorption has to include the energetic consequences of changes in metal bond energies.

The surface chemical bond consists of a distribution of electrons over bonding as well as antibonding adsorbate–surface fragment orbitals mainly involving the surface metal valence s, p and d orbitals. Usually the interaction with the s, p-valence-electron bond dominates. Differences between metals, however, are often controlled by the altered interactions with the metal d-valence electrons.

Surface properties influence the chemisorptive bond in two ways. Firstly, the electronic nature of the surface orbitals determines the splitting in bonding and antibonding surface fragment orbitals. Secondly, for a surface the Fermi level determines the amount of filling of those fragment orbitals. Interestingly, the degree of splitting into bonding and antibonding surface fragment orbitals relates to the width of the surface local electron energy density of states. This width depends strongly on the coordination number of the surface atoms involved. It provides the fundamental link between the chemical coordination approach and its electronic physical basis. The filling of the bonding and antibonding adsorbate–surface-fragment orbitals controls the strength of the adsorbate bond.

For molecules the surface chemical bond is more complex, because usually their highest occupied molecular orbitals (HOMO) as well as lowest unoccupied molecular orbitals (LUMO) interact significantly. The corresponding surface fragment orbitals have a very different distribution of electrons over bonding and antibonding fragment orbitals, which may result in counteracting effects when surface geometry or the number of surface d-valence electrons changes. When the two interactions nearly balance the preference for molecules to adsorb to specific surface metal atomic geometries is small. In section 2 we will present approximate formulae that provide a quantitative basis to the features shortly discussed here. The concept of HOMO–LUMO interactions will be generalized to surfaces and the chemisorptive electronic interactions will be related to an averaged surface local density of states. In section 3 we will present the consequences of the analysis to the relative stabilities of adsorbates chemisorbed to transition-metal surfaces.

2. Quantum chemical relations

The dependence of the local-energy density of states on metal-atom coordination number for an s-type atomic orbital follows most simply from an approximate expression; that for a body-centred cubic lattice describes the first and second moment of the density of states $\rho_{Z'}(E)$ correctly [7,11,12]:

$$\rho_{Z'}(E) = \frac{\Gamma(E)}{\left[E - \epsilon - \Lambda(e)\right]^2 + \Lambda^2(E)} \tag{1a}$$

with

$$\Lambda(E) = \frac{Z'}{2(Z-1)}(E - \epsilon), \tag{1b}$$

$$\Lambda(E) = \frac{Z'}{2(Z-1)}\sqrt{4(Z-1)\beta^2 - (E-\epsilon)^2}\,. \tag{1c}$$

Expressions for more general lattices can be found elsewhere [7]. Z' is the coordination number of the surface atom, Z is the coordination number of the atom in the bulk of the metal, ϵ is the tight-binding free metal atomic orbital energy and β the overlap energy integral. Expression (1a) is sketched in fig. 1. The most important feature of the local density of states expression is that the width is proportional to the surface coordination number and its maximum inverse to the surface coordination number.

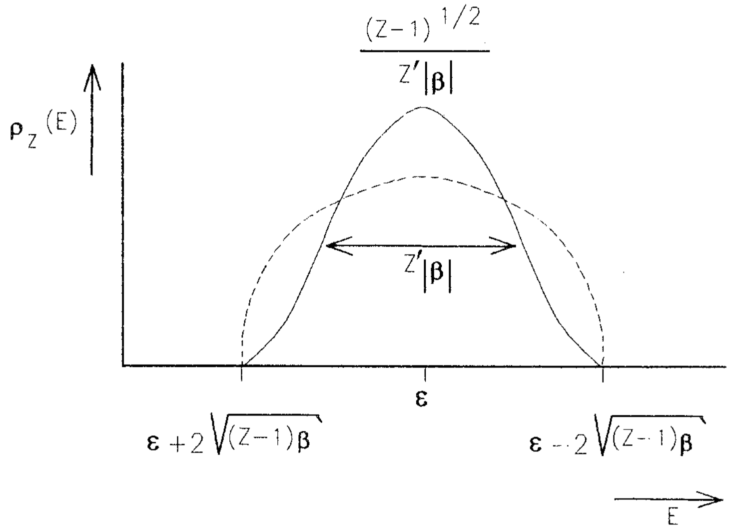

Fig. 1. The local density of states (expression (1)) as a function of energy. (——) $Z' = Z - 1$, (— — —) $Z' < Z - 1$. Z is the number of nearest-neighbour atoms in the bulk, Z' is the number of nearest-neighbour atoms on the surface.

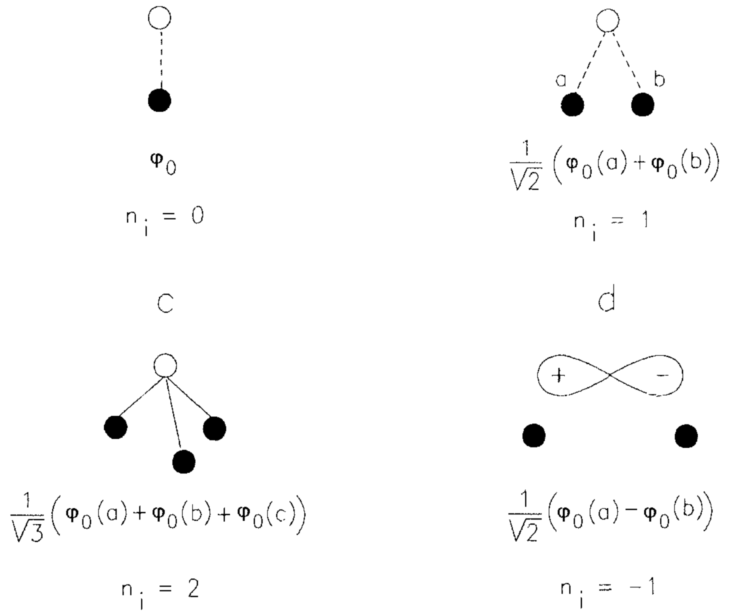

Fig. 2. (a)–(c) concern the interaction of an adsorbate s-atomic orbital o, with surface s-atomic orbitals as a function of adatom coordination number. In (d) the interaction of an adsorbate p_x orbital with surface s-atomic orbitals is given for twofold coordination. Dependent on the position the respective surface group orbitals are given.

The exact dependence of the local density of states on the energy usually is a highly variable function of the energy. However, only changes in the local density of states over an energy interval of the range of the interaction strength are of interest to the stability of the surface chemical bond. Due to the strength of this interaction details of the local density of states function are only of relevance as long as they determine its lower moments.

The electron density of states fraction that interacts with the adsorbate orbitals depends on adsorbate–surface atom coordination as well as symmetries of the interacting orbitals. For an s-type adsorbate orbital interacting with metal s-valence electrons approximated within a tight binding description this is illustrated in fig. 2. When adsorbed to a single surface atom, the adatom overlaps with the metal atomic orbital φ_0. The local density of states corresponding to this orbital is given in eq. (1). However, when adsorbed in symmetric higher coordination positions the adsorbated orbital only interacts with particular surface fragment orbitals, that are of suitable symmetry. These group orbitals are given in fig. 2 [7,11–13].

This has two consequences. Firstly, now the local density of states of the respective group orbital has to be considered; secondly, the overlap energy between adsorbate and surface atomic orbital β' found for atop adsorption becomes altered to $\sqrt{Z''\beta'}$. Z'' being the adsorbate coordination number.

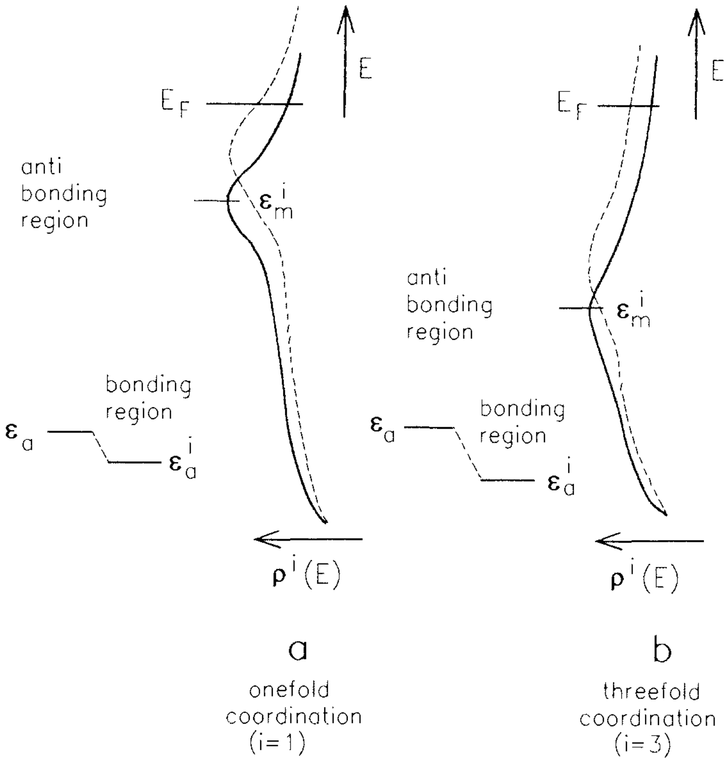

Fig. 3. Surface-chemical bonding energy diagrams. Drawn lines represent relative energies before adsorption, broken lines the shifted electron energies resulting from the interaction. At the left in each figure the shift in adatom orbital energy, at the right the corresponding changes in the surface group orbital local density of states are sketched (schematic).

The chemical bonding energy diagram for a onefold and a higher coordinated adatom with one s-atomic orbital is sketched in fig. 3. As discussed elsewhere [7,11] the local density of states of group orbitals corresponding to increasing coordination number Z'' shifts toward the bottom of the energy density distribution function. This is indicated in fig. 3. As in molecules, bonding and antibonding adatom–surface-fragment orbitals are formed. When the adatom orbital energy is lower than the maximum of the corresponding surface group orbital energy density of states (the situation considered in fig. 3), the adatom level is pushed downwards and the surface electron density of states is pushed upwards. The orbitals that participate in downwards pushed orbitals have bonding character, the ones that have been pushed upwards have antibonding character. An approximate expression for the shift of the adatom levels is

$$\epsilon_a^i - \epsilon_a = -\frac{Z''\beta'^2}{\epsilon_m + n_i\beta - \epsilon_a + Z'\beta^2/(\epsilon_m - \epsilon_a)}. \tag{2}$$

This is a conventional second-order perturbation expression for the interaction of adsorbate level ϵ_a with a cluster of metal atoms, consisting of metal atoms corresponding to the first two coordination shells of the adsorbate. The $n_i\beta$ dependence in the second term stems from the lowering of the group orbital local density of state maximum with increasing adatom coordination number. Values of n_i are given in the legend to fig. 2. Expression (2) illustrates the general result, that bonding orbitals give a larger contribution to the bond energy for adatoms with increased coordination number Z''. The interaction energy, however, decreases with increasing surface metal atom coordination number (Z').

The tight-binding orbital energy expression does not explicitly contain changes in electrostatic interactions, due to, e.g., changes in the work function. One can account for this by adding to the energy difference in the denominator of the second term in expression (2) a term corresponding to the dipole layer potential [7]. We will return to this point later.

Whereas the lowering of the bonding orbitals is always larger in high coordination sites, this is usually not the case for the antibonding levels. As illustrated

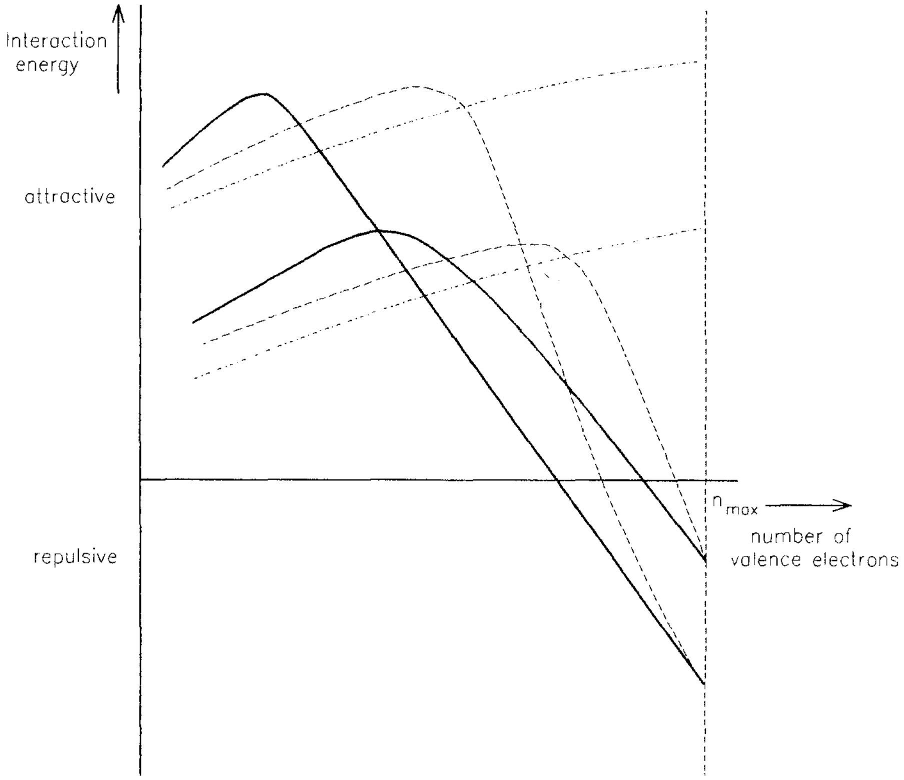

Fig. 4. The relative interaction energies of s-atomic orbitals as a function of metal-valence-electron occupation (schematic). $\epsilon_a < \epsilon_{max}$; (———) large difference between ϵ_m and ϵ_a, (— — —) small difference between ϵ_m and ϵ_a. ϵ_a^i forms part of a bonding fragment orbital set. $\epsilon_a > \epsilon_{max}$; (·—·—·) ϵ_a^i forms part of an antibonding fragment orbital set (ϵ_a^i remains empty).

in fig. 3, the antibonding orbitals have an average higher energy when adsorbates interact in low coordination sites compared to the lower energy when adsorbates interact in high coordination sites. This is due to the lower average energy of the group orbital local density of states in the latter case. Because of conservation of the total number of orbitals it implies that a larger fraction of antibonding orbitals becomes occupied in high coordination sites than low coordination sites. It tends to counteract the enhanced stabilization of the bonding orbital fragments in high coordination sites. Because the interaction energy depends on the sum of bonding as well as antibonding interactions, the overall trend in chemisorption energy may become different, than expected on the basis of considerations only of the bonding level shifts. We have found this to be the case for adsorbate orbitals when these orbitals participate significantly in occupied antibonding adsorbate–surface orbitals.

The relative dependence of the interaction energies of different coordination sites on electron occupation is sketched in fig. 4. The maximum in the interaction energy occurs when in addition to bonding levels also antibonding levels become occupied. The position of the maximum in interaction energy depends on the relative values of $\epsilon^{i}_{\max}$ and adsorbate level ϵ_{a}. When the energy of the adsorbate ϵ_{a} level increases with respect to $\epsilon^{i}_{\max}$, antibonding levels are pushed upwards in energy and the curve maxima shift to higher value of metal valence electron occupation.

One notes that there is a maximum value of the orbital occupation number below which high coordination is more stable than low coordination. When the valence-electron band becomes completely filled all orbitals of the system are doubly occupied and hence bonding becomes determined by Pauli repulsion. Within the extended Hückel approximation one finds the following behaviour as a function of adsorbate coordination number [7,14]:

$$E_{\text{Pauli}} = -Z''S\beta', \tag{3}$$

where S is the overlap of adsorbate and surface atomic orbital. When ϵ_{a} is larger than $E_{\max}$, the adsorbate orbital will now mainly participate in antibonding orbitals and be shifted upwards. Then the bonding orbitals are mainly located in the metal surface and shifted downward (see fig. 5).

The discussion has been of a qualitative nature emphasizing essential notions. For derivations of analytical expressions and a more complete analysis we refer to ref. [7]. The key results of this section, summarized in fig. 4, will be used in section 3.

3. Rules of chemisorption

The valence-electronic structure of the late transition-metal surface consists of a narrow d-valence electron band of varying electron occupation, typically

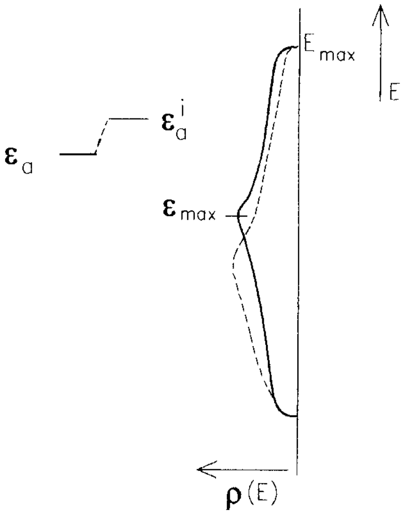

Fig. 5. Chemisorption orbital interaction scheme when $\epsilon_a > \epsilon_{max}$. Drawn lines are energies before chemisorption, broken lines are energies after chemisorption.

between six and nine electrons per metal atom. The d-valence electron band is overlapped by a broad s, p-valence electron band that has an approximate constant electron occupation of one electron per atom.

Many computational studies of chemisorption to metal surfaces or clusters simulation metal surface exist [9]. In addition analysis of semi-empirical calculations has significantly contributed to the understanding of the chemical bond of molecules, molecule fragments or atoms to metal surfaces [6].

A few general rules of chemisorption become apparent, that we will review and rationalize based on the insight provided for by the analysis presented in section 2.

One important rule concerns differences between atomic and molecular adsorption as mentioned in the introduction. Atoms as O and C are stable in high coordination positions, whereas molecules as CO do not have a strong preference for particular adsorption sites. Also the bond energies of adsorbed atoms are usually significantly larger than those of the molecules and vary much stronger with metal. Because of the large spatial extension of the metal s-atomic orbitals, interaction with these orbitals tends to dominate chemisorption energies. Differences derive mainly from the more subtle interactions with the metal d-valence electrons. Because of the many interaction possibilities provided for by the five d-atomic orbitals, interaction with the d-valence electrons is usually not restrained by orbital symmetry requirements. This is very different for interaction with s-valence electrons. When the z direction is along the surface normal, orbitals of p_x or p_y symmetry of a molecule or atom, adsorbed perpendicular to the surface plane and interacting with a single surface atom will have a zero overlap with a metal s-atomic orbital. Only in high coordination sites group orbitals, constructed of s-atomic orbitals, of proper symmetry will be available that will give a non-zero overlap with the adatom p_x or p_y orbitals. Because the atomic orbital energies of the adatom p_z, p_y and p_y atomic-valence orbitals are close to the metal Fermi level, they will mainly lead to occupied bonding adatom–surface-fragment orbitals. This favours binding to high coordination sites. This preference for high coordination sites is less for adsorbate orbitals of s-symmetry. Now a strong interaction with a surface metal s-atomic orbital is also possible when adsorbed onefold.

Due to the smaller extent of the d-atomic orbitals, the interaction with the d-valence electrons will usually be less than with the s-valence electrons. However, the small interaction with the d-valence electrons determines the difference in interaction strengths to a significant measure. The bond strength will decrease when bonding to different elements with increasing number of d-valence electrons is compared, because this will lead to an increasing occupation of antibonding adsorbate–surface-fragment orbitals. This appears to be a very general result also found for adsorption of molecules.

In general the chemical bond between molecules and the surface can be considered a combination of the interactions of doubly occupied highest occupied molecular orbitals (HOMO) and unoccupied lowest unoccupied molecular orbitals (LUMO). In the case of chemisorbed atoms the interaction with the LUMOs usually dominates. For molecular adsorption both the HOMO and LUMO interactions often are of comparable strength and tend to have opposing behaviour when differences in coordination or different metals are compared. A doubly occupied HOMO of low energy will participate in adsorbate–surface orbital fragments with a relative high electron occupation of antibonding orbital fragments. An unoccupied LUMO of high energy will participate in adsorbate–surface orbital fragments with no or low electron occupation of antibonding orbitals. Mainly bonding fragment orbitals are occupied. Because of the dominance of Pauli repulsion (eq. (3)), a strong interaction of an adsorbate HOMO orbital with a highly occupied d-valence electron band will push the molecule to a onefold position. This will minimize Pauli repulsion. The interaction with a LUMO, however, will always tend to favour high coordination sites. Now the interaction with bonding orbital fragments dominates.

In the case of CO chemisorbed at low coverage the balance of these two interactions causes CO to chemisorb preferentially in onefold coordination to metals as Co, Rh or Pt, but twofold to metals such as Ni or Pd [15]. The difference between metals Ni and Pd versus Pt is the much larger spatial d-atomic orbital extension of the latter. The interaction with the d-valence electrons in Co and Rh is larger than with those of Ni and Pd, because of their spatial extension as well as their lower d-valence-electron occupation.

As we discussed in section 2, the interaction between adatom and surface atoms decreases the larger the coordination number of the surface atoms with their neighbour metal atoms. This derives from a decreasing downward shift of the bonding adsorbate–surface orbital fragments. It is counteracted by the reverse effect on the position of the antibonding adsorbate–surface orbital fragments.

Since mainly LUMO type interactions determine the bond energy of adatoms it is more affected by changes in surface-metal atom coordination than that of molecules, with adsorbate–surface-fragment orbitals of bonding as well as antibonding character occupied by electrons. These chemical-bonding features are in line with the experimental observation of the generally enhanced reactivity of low index versus high index surfaces planes [16]. On low index planes surface atoms have a lower coordination number versus higher index plane surface atoms.

The thermodynamics of surface dissociation reactions of adsorbed molecules shifts more towards the adsorbed dissociation products, due to the larger increase in adatom than admolecule energy when the surface atom coordination number decreases. The electronic basis to the low reactivity of low index planes is the increased bandwidth of the corresponding surface local density of states (fig. 1). This is due to the increased delocalization of the metal electrons with increasing metal coordination number. The corresponding decrease in chemical reactivity can be considered related to the increase in localization energy of the surface electrons in order to form a surface chemical bond. This notion is the analogue of the bond order conservation concept [5].

In the analysis as presented here we have emphasized covalency changes in the surface chemical bond. Surfaces do not only differ in their electron-energy distributions but differ also electrostatically due to changes in charge distributions. The latter affects amongst others the relative energies of adsorbate versus surface orbitals and may sometimes dominate changes in surface chemical bonding. A classical example is the effect of alkali-atom coadsorption [17].

The work function decrease on low index planes tends to favour the interaction with the LUMO orbitals of adsorbates, hence may assist the enhanced reactivity of low index planes. The increased difference in energy of adsorbate HOMOs and surface-electronic orbitals leads to a decreased interaction, when the change in the work function dominates chemical bonding effects.

Interestingly, as we recently demonstrated for the interaction of NH_3 with Cu clusters [18], a case where the HOMO–surface orbital interaction dominates, the increased contribution to the chemical bond energy due to decreased delocalization energy dominates the loss in the interaction energy due to the altered electrostatic interactions.

4. Conclusions

Adsorbed atoms usually favour high coordination sites. Their adsorption energy decreases strongly with increased d-valence-electron occupation, due to the occupation of antibonding adsorbate–surface fragment orbitals. The adsorption energy of a molecule is controlled by the balance donating (HOMO) and backdonating (LUMO) interaction terms. Backdonation favours high coordination. Donation can favour low coordination. The interaction with the d-valence electrons controls the balance.

Bond order conservation predictions agree qualitatively with the dependence of surface atom reactivity on the surface metal atom coordination. It leads to a decreased surface atom reactivity with increasing surface electron delocalization. Bond order conservation principles are not always useful for predictions of surface coordination of molecules, because of the balance of the different interaction terms that often controls the chemical bond of the adsorbed molecules.

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