# Chapter 4

# Conclusions

Now what have we learnt from all this? We have presented the principles of a numerical method, within the density functional theory, which is nowadays in a wide use in the scientific community and with similar approaches is making its way to industrial research and development, and we believe it to establish such an important position as the quantum chemistry and eventually the small-scale semi-empirical simulations have currently there. The beauty of the density functional methods lies on the needlessness of fitting to experimental output in the calculation. Excellent examples of recent density functional calculations on industrially important catalytic reactions include the study of the rate-limiting step in the synthesis of ammonia, the dissociation of nitrogen dimer, and the effect of the alkali promoter on the the dissociation by Bjørk Hammer, Jens Nørskov and co-workers (Mortensen *et al*, 1997; Mortensen, Hammer & Nørskov, 1998); the oxidation of carbon monoxide on Pt (111), which is an important reaction in purification of the exhaust gases from the burning of fossil fuels (Alavi *et al*, 1998); the Ziegler-Natta polymerisation by Michele Parrinello and co-workers (Boero, Parrinello & Terakura, 1998).

We first gave a short overview of the method which was then applied for the calculations in the present work. This was meant to give an unexperienced reader some background to the methods used, and to clarify how the results were analysed. It also emphasises the Author's interest to the numerical approach itself, and hopefully helps newcomers to the field with thorough discussions on seldomly published issues of calculational details.

The first application of the method was to bulk ruthenium and the clean Ru (0001) surface. This provides the basis of comparison for the effects due to adsorbed species. An agreement with experiments typical for the exchange-correlation energy functional used, the generalised gradient approximation, was observed in our results, thus giving us the confidence on the approximations and calculational parameters chosen. The single adsorbate phase of cesium on the Ru (0001) was found to behave similarly to the adsorption at aluminium surfaces, and the dominating response of the surface to the adsorbate was the electric field due to the polarisation of the cesium atom upon adsorption. The field strength at typical adsorption sites for co-adsorbates exceeded 1 eV/Å, which is very strong on the chemical scale. Other alkali metals on surfaces of different transition metals were found to behave qualitatively similarly, yet the polarisation of the semi-core – $p$ – states was remarkable in the heavier alkali metals.

In the case of carbon monoxide we concentrated on the validity of the Blyholder model for adsorption at surfaces. We found there to be significant deviations from the original model, where only the highest occupied molecular orbital $5\sigma$ and the lowest unoccupied molecular orbital $2\pi^*$

would be involved in the bonding, but the overall picture of the adsorption of carbon monoxide can still be satisfactorily discussed with the Blyholder model. A significant mixing of the $4\sigma$ and $5\sigma$ orbitals within the molecule was observed. The nitrogen dimer molecule behaves similarly to the isoelectronic carbon monoxide. Further we found that the adsorption of carbon monoxide on the platinium group transition metals and copper is very delicate, and the stable adsorption site is even errorneously yielded in some cases.

The co-adsorption of cesium with the more electro-negative carbon monoxide or oxygen fitted in the general picture of the alkali being more polarised upon the adsorption, and that the interaction between the co-adsorbates is attractive – naturally they would not mix otherwise. Since the carbon monoxide and oxygen are more electro-negative than the substrate, ruthenium, the co-adsorbed alkali increased the effect seen on the adsorption of the single species. However, in the case of carbon monoxide the main effect, besides the changes due to Blyholder model, the molecule also internally polarised strongly due to the vertical electric field arising due to the alkali. The lengthening of the carbon–oxygen bond in the carbon monoxide molecule from the gas phase to the co-adsorbed one was seen to be due to three effects, first the adsorption and strengthening of the bond due to the alkali, second the electric field because of the polarised alkali and third because of the site change from on-top in the isolated phase to the three-fold hollow in the co-adsorbed structure. The latter fits in the framework of Blyholder model, where the molecule at hollow sites could fill the $2\pi^*$ orbital anti-bonding with respect to the internal molecular bond more efficiently, thus weakening and increasing the bond length. The induced density close to the Fermi energy above the cesium atom was found to behave qualitatively differently due to co-adsorption with carbon monoxide or oxygen, in a good agreement with the recent experimental results.

Since both the carbon monoxide and oxygen are usually regarded as electro-negative adsorbates it is somewhat contradictory that they do co-adsorb in a mixed structure. Yet the mixing energy is very small, and the effect of co-adsorption on the internal bond-length in the carbon monoxide molecule is to increase, opposite to the case of co-adsorption with cesium.

The results which we have presented here in length both further demonstrate the good agreement obtained with current-day electronic structure calculations with the experiments and thus give credit to the usefulness of the approach employed here, and on the other hand they provide explanations or at least hints for effects which are difficult if not even impossible to derive from experiments. Our results provide a consistent description of systems ranging from the clean (0001) surface of ruthenium to the co-adsorbed ad-species. Furthermore the adsorption of single atom or molecule has enlarged our understanding of the coverage dependence of the interactions between the adsorbate and substrate and between the adsorbates themselves. The co-adsorption systems have enabled us to gain an improved knowledge of the mechanism upon bringing the ad-particles together.

We hope that the out-come of the present work will inspire new studies on these model systems. Yet we realise the small audience which shall directly benefit from our results but hope that it acts as an initiator for wide activity on the field of the basic, some day the applied research and even industry and will eventually bring together the chemists, physicists, process analysts and industrial researchers.