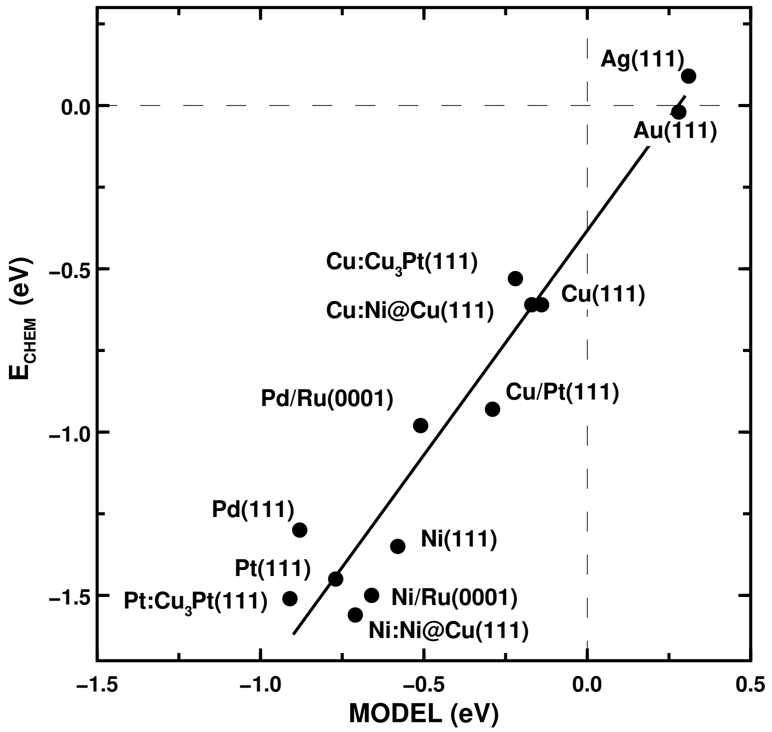

Figure 3.79: The adsorption energy of CO from the Newns-Anderson model versus the self-consistent density functional calculation in a model geometry in the $(\sqrt{3} \times \sqrt{3})$R30°-CO structure; from Hammer, Morikawa and Nørskov (1996)

the s and p electrons, in good agreement with the values for Al (111), whereas the change between different elements arises from the interaction of CO $2\pi^*$ and 5σ states with the transition metal d bands; Hammer, Morikawa and Nørskov conclude their results to be in good agreement with the prediction of the Blyholder (1964) model and the studies of Bagus and Pacchioni (1992). Hammer, Morikawa and Nørskov also discuss the correlation between the core level shifts of the transition metals and the CO chemisorption energy observed by Rodriguez and Goodman (1992) and later studied theoretically by Weinert and Watson (1995) and Hennig, Ganduglia-Pirovano and Scheffler (1997).

We finally show the changes of work function in the Table 3.19; the differences between different adsorption sites are large and although the magnitude of the changes is most likely overestimated the determination of the adsorption site based on the change in work function should still be possible. That the work function is higher at the three-fold site in all cases studied here is in line with the observation that the emptying of the 5σ orbital – located mostly at and below the carbon atom – and filling of the $2\pi^*$ – having more weight at both atoms – would shift the centre of average charge further away from the substrate, leading to an increase in the work function. Along the rows of the periodic table the change in work function decreases with the binding energy, and the change is less positive – even negative at Pt (111) – at the 5d metals than at the 4d's.

3.3.4 Adsorption of oxygen

Since the adsorption of oxygen is not central for the present work we shall here only list the main properties relative to the similar adsorption system of nitrogen on Ru (0001), which was recently studied by Schwegmann *et al* (1997). The major differences between N/Ru (0001) and O/Ru (0001)

Table 3.19: The change in work function determined by our density functional calculations upon the adsorption of CO on fcc (111) and hcp (0001) trigonal surfaces of group VIII and noble metals. The adsorption structure is always $(\sqrt{3} \times \sqrt{3})$R30°-CO. All values are in electron volts

	on-top	fcc
Cu (111)	−0.04	+0.71
Ru (0001)	+0.81	+1.22
Rh (111)	+0.55	+1.34
Pd (111)	+0.05	+1.13
Ir (111)	+0.17	+1.07
Pt (111)	−0.39	+0.93

are:

- Oxygen does not form a $(\sqrt{3} \times \sqrt{3})$R30° but a (2×1) structure; at a coverage of 1/3 rather islands of domains of (2×2) and (2×1) structures would form as is obvious from the Figure 3.80 which shows the adsorption energy at different coverages: The point at the coverage $\theta = 1/3$ lies considerably above the line joining the points at the coverages 1/2 and 1/4. Yet at the coverage 2/3 in the structure $(\sqrt{3} \times \sqrt{3})$R30°-2O our calculations yield a binding energy close to the line connecting the energy at coverages 1/2 and 3/4, and thus could be almost a stable one; however, such a structure has not been observed experimentally, and is peculiar considering the low binding energy of the similar structure $(\sqrt{3} \times \sqrt{3})$R30°
- The (2×2) is a more attractive structure than (3×3) also in our calculations and (2×2) islands of oxygen are formed in coverages less than 1/4 (Wintterlin *et al*, 1997; Nagl *et al*, 1998); the results from these scanning tunnelling microscope studies are also shown in the Figure 3.80, and regarding the possible amounts of error both in the analysis of the measurements and our calculations the agreement is very good, the remaining errors are 70 meV
- Coverages up to a full (1×1) mono-layer are stable against desorption at low temperatures as concluded from the Figure 3.80; this had been experimentally verified by low energy energy diffraction measurements in the group of Herbert Over as was suggested by density functional calculations (Stampfl *et al*, 1996). The difference between oxygen and nitrogen is not in the adsorption as the adsorption energies relative to atoms in gas phase are very similar but the large difference in the binding energy of the dimers – 9.76 eV for N_2 and 5.12 eV for O_2 – makes the desorption as N_2 preferable at much lower a temperature than in the case of oxygen

The adsorbed oxygen atom on Ru (0001) shows the same, although smaller, trend of shortening adsorption bond distance as recently found by Schwegmann *et al* (1998) on the Ru $(10\bar{1}0)$ surface: whereas oxygen-ruthenium distance shortens by 0.05 Å from the Ru $(10\bar{1}0)$-c(2×4)-2O to Ru $(10\bar{1}0)$-(2×1)-*p2mg*-2O on the Ru (0001) surface this distance in the (1×1) structure is shorter by 0.03 Å than in the (2×2) structure. However, the densities in these structures on the two different surfaces are smaller by about a factor of two which makes the comparison somewhat more complicated.

We did a similar analysis to extract the parameters for the two and three particle potentials as was done for carbon monoxide on Ru (0001) in the Section 3.3.2; the results are collected into the Table 3.20. Although the agreement between the analysis between the parameters from the analysis of scanning tunnelling microscope images and the density functional calculations is not very good

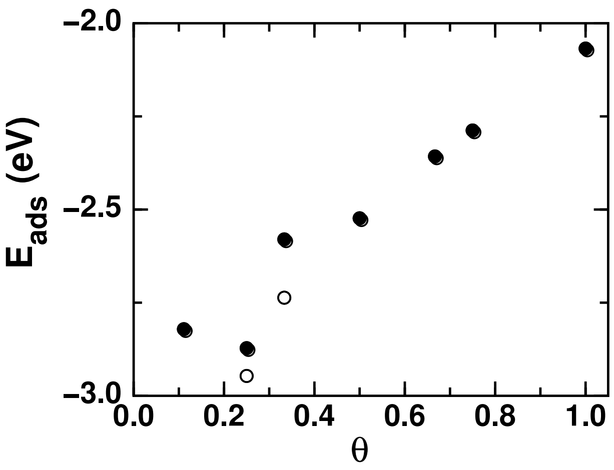

Figure 3.80: The adsorption energy of oxygen on Ru (0001) from our density functional calculations – filled circles – and derived from the statistical distribution of atom in the scanning tunnelling microscope measurements by Wintterlin *et al* (1997) and Renisch *et al* (1999) – open circles – in different ordered structures. The energies are calculated with respect to O_2 molecule in the gas phase, and the experimental values are normalised to be equal to the calculations in the (3×3) structure

Table 3.20: The two- and three-particle interaction parameters for oxygen on Ru (0001) extracted from density functional calculations by us and Stampfl *et al* (1999), and from a statistical analysis (Renisch *et al*, 1999) of atomic jumps observed with the scanning tunneling microscopy; the parameters have been defined like in the Figure 3.58 except that here (3×3) structure was regarded as isolated and V_2" is the pair-wise interaction energy between adsorbates at the third-nearest neighbour sites; all values are in electron volts

	E_0	V_2	V_2'	V_2"	V_t	V_t'
DFT	−2.821	0.371	0.080	−0.017	0.063	−0.103
Stampfl	−2.503	0.265	0.044	−0.025	0.058	−0.085
STM			0.028	−0.042		

it is important to realise that the experimental values correspond to binding or attachment energies at island boundaries rather than the binding energies in ordered layers like we have used them here.

We made still a qualitative study about the change work function upon the adsorption of electronegative atoms and the NH molecule on the Ru (0001) surface. The result in the Figure 3.81 shows interesting differences between the adsorbates: for example whereas the change for oxygen and the iso-electronic sulphur is positive and about of the same magnitude but as nearest-neighbour sites start to be occupied the work function for sulphur starts to decrease; although the high coverages of sulphur have not been produced experimentally to the best of our knowledge they might be possible since the atomic and covalent radii of sulphur are smaller than half of the nearest-neighbour distance on Ru (0001); we have obtained a binding energy in the excess of 1.5 eV in the (1×1)-S structure. The change in the work function of oxygen within the local density approximation is smaller than in the generalised gradient approximation and thus closer to the experimental values. The change in the case of oxygen is very similar to the one induced by nitrogen, except that at high

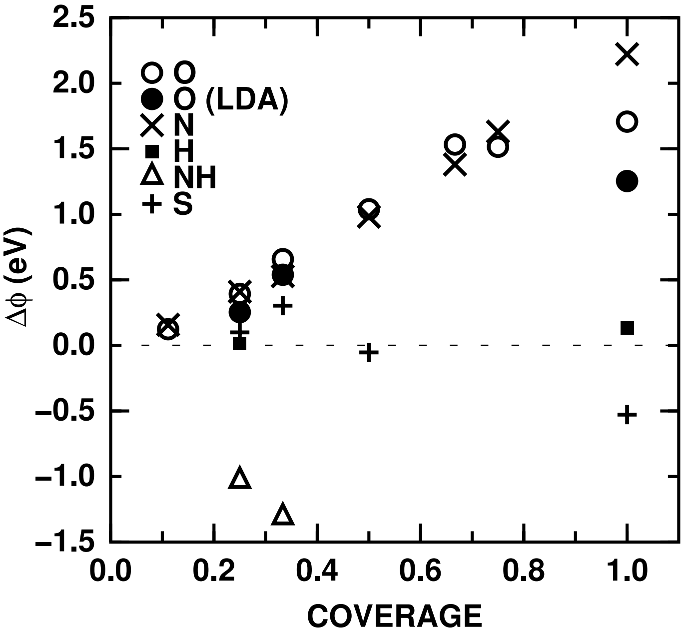

Figure 3.81: The change in work function upon adsorption on Ru (0001) for several electro-negative species; oxygen has been calculated both with the local density and generalised gradient approximations, all the other calculations (Ari P Seitsonen, unpublished results) were done employing the generalised gradient approximation

coverage the change for oxygen levels off but continues for nitrogen.

3.4 Co-adsorption on Ru (0001)

As mentioned in the Introduction the co-adsorption is extremely important since in the Langmuir-Hinshelwood mechanism of the catalytic reaction the reactants, in addition to the possible promoters and inhibitors, adsorb to the surface prior to the reaction. A recent review which covers the structural and electronical aspects of co-adsorption has been published by Herbert Over (1998). Here we shall present our calculated results for three different co-adsorption system where two of the adsorbates of the previous Section, cesium, carbon monoxide and oxygen, are combined at the Ru (0001) surface at a time. This gives us an opportunity to monitor the changes on the adsorbates when they are exposed to a chemically different species on the surface; also the important reactants and test molecule carbon monoxide is combined with the electro-positive cesium and the electro-negative oxygen, which is also the other reactants in the oxidation process of the CO.

3.4.1 Co-adsorption of cesium and oxygen

The co-adsorption of alkali and oxygen atoms has been widely studied (Surnev, 1989). One interesting occurrence of the system is in the ammonia catalysts as discussed *e.g.* by Ertl (1991). On Ru (0001) the co-adsorbed cesium and oxygen has been the subject of studies employing the low energy electron diffraction (Over *et al*, 1992a; Bludau *et al*, 1995; Trost, Wintterlin & Ertl, 1995), scanning tunnelling microscope (Trost, 1995; Trost, Wintterlin & Ertl, 1995) and high-resolution electron energy loss spectroscopy (Jacobi *et al*, 1995). With cesium as very electro-positive and oxygen electro-negative atom the interaction between them is attractive but the repulsion between like