

AB-INITIO CALCULATION OF THE INITIAL- AND FINAL-STATE  
EFFECTS ON CORE LEVEL SHIFTS AT TRANSITION METAL  
SURFACES

D. HENNIG\*, M. METHFESSEL<sup>†</sup> and M. SCHEFFLER<sup>†</sup>

\*Humboldt-Universität zu Berlin, Institut für Theoretische Physik, Invalidenstr. 110  
O-1040 Berlin, Germany

<sup>†</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, W-1000 Berlin, Germany

The surface core-level shift at a transition metal surface can be calculated in two different ways using the initial-state approximation or using a more involved approach which includes screening of the photo-created core hole. Our calculated results obtained using the full-potential LMTO method for the close packed surfaces of all 4d transition metals within the initial state picture can be well explained by standard arguments.

The surface core-level shift (SCLS) of the transition metals is a field of experimental interest over many years, especially for the 5d metals a survey of data has been collected in references 1 and 2. For the 4d metals a smaller amount of data is available.

For the calculation of the SCLS an ab-initio total energy method (in our case the full-potential linear muffin-tin orbital, FP-LMTO, method<sup>3,4</sup>) can be used. We have modeled the surface by slabs of seven layers. In the initial-state approximation the SCLS is identified with the shift of Kohn-Sham eigenvalues of the core states relative to the bulk. The atoms in the central layer of the slab are taken as identical with bulk atoms. In a more correct approach one should taken into account that valence electrons will relax to screen the photo-created core hole. In a metal one electron wanders in from infinity to re-attain local charge neutrality. It is the total-energy change of this electronically relaxed system respective to the unperturbed surface which is imparted to the emitted electron. Since screening could be different at the surface and in the bulk, an effect on the SCLS is possible. In the following, we denote approaches which attempt to include the electronic relaxation effects in some way as "final-state" theories. In order to take these many-body screening effects into account we use the equivalent-core approximation<sup>5</sup> in which the atom with the deep core hole in a crystal of atoms with the atom number  $Z$  is approximated by an impurity atom with an atom number of  $Z + 1$ . The SCLS then equals the total-energy difference of impurity calculations of a  $Z + 1$  impurity in the central layer of the slab and at the surface. The impurity-host system is modeled by a supercell in which either the central layer or the two surface layers contain 25%  $Z + 1$  atoms.

In the context of total-energy calculations based on the local-density approximation<sup>6</sup>, the connection between the initial- and final-state description can be studied<sup>7</sup>. The total energy is a function of the core-level occupation which can be taken as a continuous variable. The derivative of the LDA total energy respective to the occupation number equals the corresponding eigenvalue. Consequently the initial-state theory is the first-order term in a Taylor series in the change of the core charge, whereas the final-state description includes the terms to all orders. A review of theories for the SCLS can be found in reference 2.

Below we report initial-state results for the close packed surfaces of all the 4*d* transition metals and final-state calculations for Mo and Rh.

In the initial-state approximation the SCLS of metal surfaces is understood to originate mainly from the local density of state (DOS) narrowing for surface layer atoms (due to a reduced numbers of neighbors) compared to the local DOS of the atoms in the bulk re-attain layerwise charge neutrality, the electrons rearrange slightly, causing an extra electrostatic potential at the surface atoms. The valence electron redistribution shifts the deeper core levels by this potential. For metals with the number of *d* electrons  $N_d$  smaller than 5 this effect would produce a deeper core level (with a higher binding energy - a negative SCLS) and in the case of  $N_d > 5$  it would appear as a positive SCLS; that is the core states of the surface atom more higher and the binding energy becomes smaller. Following tight-binding arguments, the width of the local DOS would be proportional  $\sqrt{C}$ , where  $C$  is the number of nearest neighbor bonds of the atom<sup>8</sup>. The SCLS is given by the formula<sup>8</sup>

$$\Delta = \left(\sqrt{\frac{C_s}{C_b}} - 1\right)W \frac{N_d - 5}{10} \quad (1)$$

where  $C_s$  and  $C_b$  are the coordination number for surface and bulk atoms, respectively, and  $W$  is the width of the valence band. This equation was used to compare the calculated result for different surfaces of one and the same fcc 4*d* metal. For close packed surfaces eq. (1) gives the ratios  $\Delta_{100}/\Delta_{111} = 1.37$  and  $\Delta_{110}/\Delta_{111} = 1.763$ . Using these numbers, we show in Fig.1 the normalized SCLS for the 1*s* states in the initial-state description. Two basic features are visible. First, the SCLS increases across the series, going through zero when the *d* band is approximately half full. Second, the SCLS increases with the roughness of the surface. The figure shows that the surface dependence is well-described by the tight-binding model, clearly because this theory properly estimates the narrowing of the surface DOS when bonds are cut. The linear relation in eq. (1) for the SCLS as function of  $N_d$  is qualitatively correct, but it does not describe the flattening of the curve found in the correct calculation at large *d* occupations.

A comparison to the available experimental values shows acceptable agreement with the results of initial state calculations. The measured SCLS for the 4*p* state and Y hcp(0001) is between -0.7 and -0.9 eV<sup>9</sup>, comparable to our calculated value of -0.5 eV for the fcc(111) surface. For the 3*d* state of the Pd fcc(100) surface the experimental result of 0.44 eV<sup>10</sup> agrees with the calculated result of 0.47 eV. For the 3*d* state and the Mo bcc(110) surface, a SCLS of 0.33 eV has been measured<sup>11</sup>. The calculation for the bcc(110) surface gives 0.14 eV for this state, whereby the surface with the calculated inward relaxation of 3.9%<sup>4</sup> was considered. Note that the calculated shift for the 1*s* state is even smaller, namely 0.06 eV. Furthermore, we point out the interesting result that the SCLS of Mo has different signs for fcc and bcc surfaces.

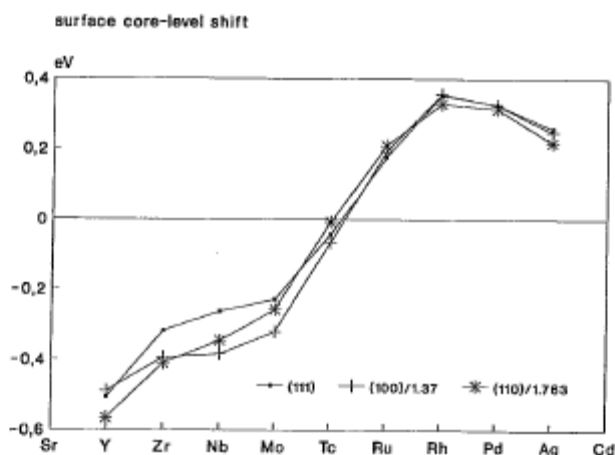


Figure 1. Calculated surface core level shift for the 1s level using the initial-state approximation. Results are shown for the non relaxed low-index fcc-surfaces, normalized according to eq. (1).

Results for close packed fcc surfaces of Rhodium are compared to other ab-initio-calculation<sup>12</sup> in table 1.

Table 1: Calculated SCLS for Rhodium (non relaxed surfaces) in the initial state approximation for the 4s state.

		Feibelman/Hamann <sup>12</sup>	our results
Rh(100)	1.layer	0.75 eV	0.57 eV
	2.layer	0.05 eV	-0.03 eV
Rh(111)	1.layer	0.46 eV	0.40 eV
	2.layer	-0.05 eV	-0.05 eV

The ratios of  $\Delta_{100}/\Delta_{111}$  for the surface layer values are 1.63<sup>12</sup> and 1.43, respectively, compared to the ideal value (according to (1)) of 1.373. Agreement of the calculated results with different methods are acceptable but not ideal. Further work is needed to find the responsible factors; candidates are the slab-separation distance, relativistic effects, and basis-set convergence.

In the second approach we used the equivalent-core approximation which is based on the assumption that the valence electrons are insensitive to the differences between an extra nuclear charge and the presence of a core hole. This approach is here implemented into an impurity calculation, considering a  $Z + 1$  atom (in place of the atom with the photo-created core hole) in the central layer of the supercell and in the metal top layer.

For the Mo bcc(110) surface we found a SCLS of 0.11 eV compared with the initial state approximation result for the 1s state of 0.06 eV, but both results differ significantly from experimental result of 0.33 eV measured for the 3d state. In the equivalent core approximation no core-state dependence is considered, but of course the  $Z + 1$  description is more appropriate for the 1s state than for the 3d state. If the spread of 0.08 eV between the SCLS for different core states of the Mo bcc(110) surface is assumed to be given correctly by the initial-state approximation and is added to the final state result one gets a value of 0.19 eV for the equivalent-core approximation in somewhat better agreement with experimental results. For the Rh fcc(100) surface we found that the SCLS for the equivalent-core approximation (0.55 eV) agrees well with the initial-state result (0.51 eV for the 1s and 0.59 eV for the 3d state).

### References

1. P.H. Citrin, and G.K. Wertheim, *Phys. Rev.* **B27** (1983) 3176.
2. D. Spanjaard, C. Guillot, M.C. Desjonqueres, G. Treglia, and J. Lecante, *Surf. Sci. Rep.* **5** (1985) No 1-2.
3. M. Methfessel, *Phys. Rev.* **B38** (1988) 1537, M. Methfessel, C.O. Rodriguez, and O.K. Andersen, *Phys. Rev.* **B40** (1989) 2009.
4. M. Methfessel, D. Hennig, and M. Scheffler, *Phys. Rev.* **B46** (1992) 4816.
5. A. Rosengren and B. Johansson, *Phys. Rev.* **B23** (1981) 3852.
6. L. Hedin and B. I. Lundqvist, *J. Phys. C* **4** (1971) 2064.
7. A. R. Williams and N. D. Lang, *Phys. Rev. Lett.* **40**, (1978) 954.
8. M. Lannoo and P. Friedel: *Atomic and Electronic Structures* (Springer, Berlin, 1991).
9. R.G. Jordan, A.M. Begley, S.D. Barrett, P.J. Durham, and W.E. Temmerman, *Solid State Commun.* **76** (1990) 579.
10. R. Nyholm, M. Qvarford, J.N. Andersen, S.L. Sorensen, and C. Wigren, preprint.
11. J.N. Andersen, private communication.
12. P.J. Feibelman and D.R. Hamann, *Phys. Rev.* **B28** (1983) 3092.