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Ab-initio calculations of the initial- and final-state effects on the surface core-level shift of transition metals

M. Methfessel, D. Hennig [1] and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-14195 Berlin, Germany

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The surface core-level shift (SCLS) can be obtained from density-functional theory calculations in two quite different ways. First, in an "initial state" approximation, the SCLS is taken equal to the difference of the core levels of the surface and bulk-like atoms in a self-consistent calculation for the unperturbed surface. Second, in a more involved "final state" theory, the effect of the core hole is included by comparing calculated total energies for a $Z+1$ impurity at the surface and in the bulk. The second approach takes into account the possibly different screening of the core hole near the surface, but has the disadvantage that it involves an expensive calculation for a surface impurity. We present calculated SCLS for some typical transition metals using the full-potential LMTO method and both approaches. The results for the smoother surfaces of all 4d transition metals within the initial state picture can be well explained using a standard model based on narrowing of the surface atom density of states and local charge neutrality. The comparison of initial- and final-state calculations is used to draw conclusions about the nature of the screening in d and sp metals.

Core levels are sensitive to the distribution of the valence electrons, and therefore to the environment of the atom. Since synchrotron radiation has become available as a research tool, there has been a large increase in the spectroscopy of core levels as a probe for surface properties. The measured values of the surface core-level shift (SCLS) need theoretical support in order to achieve an analysis about the surface. In general terms, two complementary approaches are possible. In the "initial state" description, the calculated core levels, as obtained from a self-consistent all-electron calculation, are identified with the core electron orbital eigenvalues. This is a straightforward procedure, but it neglects screening effects which might well be important. When an electron is removed from a core state without permitting the other electrons to relax, a charged impurity results. In a metal the valence electrons will relax to screen the extra charge, whereby one electron wanders in from infinity to re-attain local charge neutrality. It is the total-energy change of this 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 a total energy calculational method, the relaxation effects can be obtained directly, albeit with some effort, by using impurity calculations [1]. If Z is the nuclear charge of the metal, let Z^* denote the atom with a core hole in some selected core state. Calculations are done for the total energies of a Z^* impurity at the surface and in the bulk of the Z host. The SCLS is then the difference of the two total energies. This energy difference is in fact the heat of surface segregation for such an impurity [2,3]. As an additional simplification, one can now invoke the "equivalent core" [3] or "$Z+1$" approximation

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[1] Permanent address: Department of Theoretical Physics, Humboldt-University of Berlin, Invalidenstrasse 110, D-10115 Berlin, Germany.

[2,4]. This assumes that the effect on the valence electrons of de-occupying a low-lying core state is essentially the same as increasing the nuclear charge by one. Thus, possible effects due to the spatial extension of the core state as well as the influence of core–core and core–valence exchange–correlation are neglected. The SCLS for, say, a Pd surface then reduces to the surface segregation energy of a Ag impurity in the Pd host.

In the context of total-energy calculations, based on the local-density approximation [7], the connection between the initial and final-state description can be made [8]. The total energy is a function of the core-level occupation which can be taken as a continous variable. The derivative of the LDA total energy, respective to the occupation number, equals to 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. Furthermore, by means of a transition-state argument [5] the SCLS (including final-state relaxations) should be obtained to a good approximation by the core levels for occupations of one-half of an electron in the considered core state. A comprehensive and useful review of theories for the SCLS can be found in ref. [9].

In the calculations presented here, answers are sought for two questions: first, whether electron relaxation effects make an important contribution to the SCLS for transition metal surfaces, and secondly, to what extent the $Z+1$ approximation is valid. The second point is coupled to the question of whether the SCLS is the same for the different core states. The calculations were done using the full-potential linear muffin-tin orbital (FP-LMTO) method as applied to transition metal surfaces in the slab geometry [11]. The method permits a completely general shape for the potential and charge density in all parts of space. For calculation of the core states, it is sufficient to use the spheridized potential within the muffin-tin spheres, since the splitting of the levels by the non-spherical potential terms is of no interest. The slabs consisted of seven layers; the impurity systems were treated by the supercell technique with a four times larger cell in the surface plane in order to model the isolated impurity. Other details of the calculations are as those described in ref. [11]. Initial-state results were obtained for the smooth surfaces of all the 4d transition metals and final-state calculations were done for Mo, Rh, Pd and Ag.

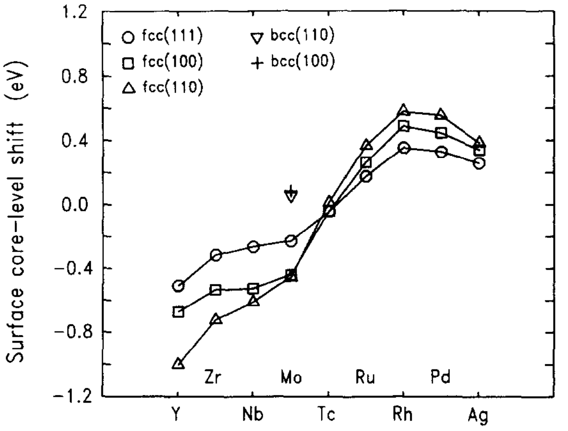

Fig. 1. Calculated 1s surface core-level shifts in the initial-state approximation across the 4d series for different low-index surfaces.

First, we consider the SCLS as obtained from the initial-state description. Here, and in the following, we follow the convention that a positive SCLS means that the surface core eigenvalue lies above that of the bulk. We warn that a number of workers consider core binding energies (as positive numbers) instead, leading to the opposite sign convention. Fig. 1 presents the calculated shifts of the 1s states for the 4d metals. In overall terms, two basic features are visible. First, the SCLS increases across the series, going through zero when the d band is approximately one-half full. Secondly, the SCLS increases with the roughness of the surface. Both features have been understood in a simple model [6]. Due to reduced coordination at the surface, the local density of states (DOS) for a surface atom is narrower compared to that of a bulk atom. The amount of narrowing is determined by the number of cut bonds of a top-layer atom, which are 3, 4 and 5 for the fcc (111), (100) and (110) surfaces, respectively. If the surface and bulk DOS do not shift relative to each other, a charge transfer to the

Table 1
Calculated surface core-level shifts (in eV) in the initial-state theory for various 4d metals for the different core levels; results are for the unrelaxed fcc (100) surface in all cases except for Mo, where the values refer to the unrelaxed bcc (110) surface

State	Mo	Tc	Ru	Pd	Ag
1s	0.01	−0.11	0.33	0.41	0.32
2s	0.08	−0.10	0.43	0.48	0.36
2p	0.07	−0.02	0.42	0.47	0.36
3s	0.09	−0.03	0.42	0.47	0.36
3p	0.09	0.00	0.42	0.47	0.36
3d	0.09	0.00	0.43	0.47	0.36
4s	0.16	0.06	0.43	0.44	0.33

surface atoms would result which is negative at the start of the transition metal series, zero for a half-full band and positive near the end. Charge will redistribute slightly to re-attain charge neutrality, leading to an extra potential on the surface atom which shifts the surface DOS. To the first approximation, the extra potential is a constant Madelung shift of the surface atom potential, shifting the core states in the same way as the valence electron DOS. In this framework, tight-binding theory has been used to derive expressions for the SCLS [10] as

$$\Delta = \left(\sqrt{\frac{Z_S}{Z_B}} - 1\right)\left(\frac{N_d - 5}{10}\right)W, \tag{1}$$

where Z_S and Z_B are the coordination numbers for surface and bulk atoms, N_d is the number of d electrons, and W is the width of the d band. The expression can be used to normalize the surface-dependent core-level shifts of fig. 1, with the result that the curves are almost superimposed. This 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 at large d occupations in the calculation.

We now turn to the question of whether the SCLS is the same for all the core states of an atom. In table 1, the dependence of the SCLS on the selected core state for the unrelaxed surfaces is shown. These typical cases show the characteristic behaviour found in the calculations, that the spread in the shifts is small at either end of the series and rather large near the middle. This correlates with the charge transferred away from the surface atom, which we have calculated to be approximately parabolic across the series and reaching values of about 0.3 electrons near the middle. This charge transfer, which remains despite the shift of the surface DOS, can have the effect of shifting the core levels non-uniformly. For this to happen, it is neccessary that the screening charge overlaps the density of the core state to some extent, which will be the case. Depending on the size of a core state, it will be affected to a varying amount. If the surface is permitted to relax inward [11], the spread of the core shifts tends to reduce. This indicates that the charge deficit on the surface atom is also decreased by the relaxation.

A comparison to the available experimental values shows acceptable agreement. The measured SCLS for the 4p state in hcp Y(0001) [12] is between −0.7 and −0.9 eV, comparable to our calculated value of −0.5 eV for the fcc(111) surface. For the 3d state of the Pd(100) surface the experimental result of 0.44 eV [13] agrees with the calculated result of 0.47 eV. For the 3d state and the Mo bcc(110) surface, a SCLS of 0.33 eV has been measured [14]. The calculation gives 0.14 eV for this state, whereby the surface with the calculated inward relaxation of 3.9% [11] was considered. Note that the calculated shift for the 1s 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.

Turning to the "final state" calculations in the $Z+1$ approximation, table 2 displays the calcu-

Table 2
Comparison of intial- and final-state $Z+1$ surface core-level shifts with experiment (in eV)

Surface	Initial 1s	Initial 3d	$Z+1$	Exp 3d
Mo(110) bcc	0.06	0.14	0.11	0.33
Rh(100) fcc	0.51	0.59	0.55	–

lated results for Mo and Rh and compares with available exerimental data for Mo. Here, we see the unexpected results that the $Z+1$ theory does not improve agreement in the case of Mo. To explain this fact, we adopt the commonly made assumption that the $Z+1$ theory corresponds to a core hole in the 1s state, but not necessarily to one in a higher core level. Assuming that the spread between the SCLS for the different states is given correctly by the initial-state theory, we can add 0.08 eV to the $Z+1$ value, obtaining an estimate of 0.19 eV for the 3d state in somewhat better agreement. To verify this explanation, self-consistent calculations are needed which make a real core hole in the considered core level. For Rh, the initial- and final-state calculated results agree well, as could be expected from the smaller spread of the core levels near the ends of the transition metal series. The $Z+1$ description for Pd is interesting because the $Z+1$ construction turns Pd into Ag, which is qualitatively different because the d band is filled. Let Δn_c be be the charge taken from a selected core state, considered a continuous variable ranging from zero to one. Due to the screening by the valence electrons, the removed core charge is put into the valence DOS. It is reasonable that for small values of Δn_c, this charge goes into the d valence band for the atom with the core hole. For larger values, the extra charge will go either into the sp state of the same atom or into d states on the neighboring atoms. Either way, it can be expected that the character of the screening then changes, affecting the various core states in different ways. As a first consequence, the convergence with the size of the supercell in the plane (needed to isolate the impurities) is much slower. Calculations are under way to obtain the final-state SCLS for Pd using larger supercells. Finally, measurements for polycrystalline Ag films have deduced a very small SCLS for Ag [15], in disagreement with our initial-state result. Therefore, Ag is also a candidate for a system in which final-state effects could be significant.

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