Trends in adsorbate induced core level shifts

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ABSTRACT

Photoelectron core level spectroscopy is commonly used to monitor atomic and molecular adsorption on metal surfaces. As changes in the electron binding energies are convoluted measures with different origins, calculations are often used to facilitate the decoding of experimental signatures. The interpretation could in this sense benefit from knowledge on trends in surface core level shifts for different metals and adsorbates. Here, density functional theory calculations have been used to systematically evaluate core level shifts for (111) and (100) surfaces of 3d, 4d, and 5d transition metals upon CO, H, O and S adsorption. The results reveal trends and several non-intuitive cases. Moreover, the difficulties correlating core level shifts with charging and d-band shifts are underlined.

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1. Introduction

X-ray photoelectron spectroscopy (XPS or ESCA) is a standard technique for chemical analysis that offer site and element specific information [1]. With high resolution X-ray photoemission spectroscopy (HRXPS), shifts smaller than 0.1 eV can be detected, and it is possible to separate surface and bulk components for metal surfaces [2]. In this way, HRXPS is often used in combination with diffraction techniques or scanning probe microscopy for structural determinations of complex surfaces [3–6]. By the development of differential pumping techniques [7] it is, furthermore, possible to follow changes of metal surfaces during chemical reactions. However, as similar core level binding energies, in principle, could have different origins it has proven helpful to compare experimental signatures with predictions of models for core level shifts (CLSs) [8–10] or explicit first principles calculations.

The basis of XPS is the response of core electrons to changes in the valence region, such as different types of charge transfer and re-hybridization. Traditionally, shifts in core level binding energies have been interpreted by the use of electrostatic arguments [8,11,12]. In such models, the shift of a core state at site i could schematically be described by:

$$\Delta E_i = \Delta\left(kq_i + \sum_{j \neq i} \frac{q_j}{R_{ij}} \right).$$ (1)

Here, q_i is the net charge on atom i, k is the Coulomb repulsion integral between core and valence states [9] and R_{ij} is the distance between the nuclei i and j. A positive (negative) shift is predicted in cases where the net charge on the site of interest is positive (negative). The change in on-site electrostatic potential is one part of what generally is referred to as initial state effects. The initial state effects may also include changes in the Fermi energy, intra-atomic charge transfer, and charge redistribution owing to bond re-hybridization [11,13]. As the lifetime of the core hole generally is long with respect to the photo-emission process, experiments measure the binding energies including electronic relaxation (screening) around the created core-hole. This relaxation (ΔE_i^r) is commonly referred to as a final state effect. A more complete representation of the core level shift E_i^{CLS} is consequently:

$$E_i^{CLS} = \Delta E_i - \Delta E_i^r.$$ (2)

Over the years, the importance of final state effects has been stressed for various systems [13–16]. Allowing for complete screening results in the, so called, impurity model were the core-ionized Z atom is replaced by an impurity with a $Z + 1$ nucleus [17,18].

Despite the fact that it generally is difficult to decouple different contributions to the measured core level shifts first principles calculations have been shown to be an important tool to rationalize measured shifts [11,19]. In particular, calculations based on the Density Functional Theory (DFT) have been shown to be able to reproduce experimental CLSs of metallic systems with reasonable accuracy. One reason for this success is the insensitivity of calculated shifts to details in the exchange-correlation functional [20–22]. This is related to cancelations of errors based on the localized nature of the core state. However, it should be noted that the functional may have a pronounced effect for oxides where the self-interaction error in gradient corrected functionals underestimate the charge separation [23,24].

In order to enhance the understanding of core level shifts on metal surfaces it is instructive to study trends across the periodic table. Previously, this has been done mainly for bare metal surfaces [19,25–28], or for a limited number of adsorbates [29,30]. Here, we present a DFT study addressing a range of 3d-, 4d- and 5d-metals and

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focus on the core level shifts upon adsorption of CO, H, O and S. Results are presented for close-packed surfaces together with the (100) facet for the fcc metals. The results reveal several interesting effects where one example is a reversed (negative) core level shifts upon O adsorption on Cu, Ag and Au. The calculations are analyzed with respect to charge transfer and the d-band centers.

2. Computational method

The density functional theory is used as implemented in the VASP code [31–34] using the gradient-corrected Perdew, Burke, and Ernzerhof (PBE) approximation to the exchange-correlation functional [35]. Spin-polarization is included in the case of Ni and the gas-phase molecules. Standard PBE Projector Augmented Wave (PAW) potentials [36,37] are used to describe the interaction between the valence electrons and the core. The number of electrons treated in the valence for the considered elements are H(1); C(4); O,S(6); Ru(8) Co, Rh, Ir(9); Ni, Pd, Pt(10); Cu, Ag, Au(11); Cd(12). The kinetic energy cut-off for the plane-wave basis set is set to 420 eV which ensures sufficient convergence for the considered potentials and elements. Reciprocal space integration over the Brillouin zone is approximated with finite sampling using Monkhorst-Pack grids [38,39] corresponding to $11 \times 11 \times 11$ in the unit cell of bulk metals. Gas-phase molecules are treated in a cubic cell with side 12 Å using only the Gamma point. The binding energies of the gas phase molecules are calculated (measured [40]) to be 4.53 (4.48), 6.06 (5.11) eV, 5.00 (4.37) and 11.64 (11.09) eV, for H_2 O_2, S_2 and CO, respectively. The severe over-binding of O_2 is a well known consequence of the applied approximation of the exchange-correlation functional [35].

The close-packed surfaces [(111) for fcc-metals and (0001) for hcp-metals] are considered for all metals together with the (100) facet for the fcc metals. In all cases, $p(2 \times 2)$ surface cells are employed with a k-point sampling of $(7 \times 7 \times 1)$. Adsorption energies are evaluated with a slab of five atomic layers, whereas nine layers are used for calculations of core level shifts. The vacuum spacing between repeated slabs is at least 14 Å. Geometry optimization is performed without any constraints and the structures are considered relaxed when the largest force in the system is smaller than 0.01 eV/Å.

The core level shifts (CLSs) are calculated including screening of the core hole [41]. In this approach, the CLS is calculated as a total energy difference between a core-ionized atom either in the surface or in the bulk of the slab. The approach assumes (i) that the lifetime of the core hole is long with respect to the photo-emission process, (ii) that the system is in the ground state with the constraint of a core hole, and (iii) that structural relaxations are negligible. These approximations are valid for the systems considered in the present study. The core-ionized atoms are obtained by generating a PAW potential with an electron hole in either the 2p-orbital (3d-metals), 3d-orbital (4d-metals) or the 4f (5d-metals). As the periodic boundary conditions exclude the use of charged super-cells, charge neutrality is maintained by adding an extra electron to the valence.

3. Adsorption energies

Trends in adsorption energies of small molecules and atoms have been studied extensively in the past [42]. Here we report the calculated adsorption energies merely as a check of the computational procedure and to put the calculated CLS in relation to the stability. Adsorption of H, CO, O and S is considered on the close-packed [(111) or (0001)] and (100) surface. The preferred adsorption configuration was investigated by probing atop, bridge, fcc-hollow and hcp-hollow on (111) and atop, bridge and hollow on (100). The adsorption energies are calculated with respect to the gas phase molecules H_2, O_2, S_2 and CO. Negative adsorption energy indicate exothermic adsorption. Adsorption was considered at two coverages, namely $\theta = 0.25$ and $\theta = 0.5$.
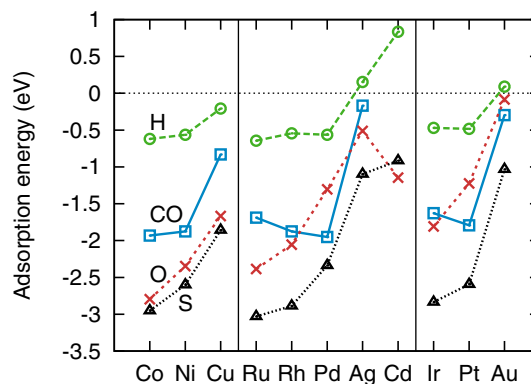

Fig. 1. Adsorption energies for H_2, CO, O_2 and S_2 in fcc position on the investigated close-packed surfaces.

The adsorption energies for the fcc sites at a coverage of 0.25 are reported in Fig. 1. The fcc site is not the preferred site for all combinations of metals and adsorbates. However, the difference between the other sites is within 0.2 eV, with the exception of CO adsorption on Ir(111) where the top configuration is preferred over fcc by 0.47 eV and O and S adsorption on Ru(0001) where the hcp site is favored. Adsorption energies for all investigated sites and surfaces are given in the Supporting information.

The lowest adsorption energies are calculated for hydrogen, whereas sulfur experiences the highest binding energy. Within a row in the periodic table, metals with open d-shells have similar binding energies for H and CO, whereas a clear reduction of the binding energies are predicted for the noble metals Cu, Ag and Au. For oxygen and sulfur, the adsorption energies decrease monotonically with filling of the d-bands. The difference in trends for H and CO on one hand and O and S on the other exemplifies the differences in the bond character between reducing and oxidizing adsorbates. A clear trend between the 3d-, 4d-, and 5d-metals rows are present only in the case of oxygen adsorption [42].

The trends for the adsorption energies calculated for the close-packed surfaces are valid also for (100). The adsorption energies for this surface are given in the Supporting information. In general, the adsorption energies are slightly larger for the open surface, although some exceptions exist.

4. Convergence of SCLS

Turning to the core level shifts, we start by investigating the convergence of the results with respect to the number of layers in the slab. As the bulk reference is modeled with an atom in the center of the slab, it is important that the slab is thick enough to ensure that the reference atom experiences a bulk environment also in the presence of an adsorbate. The slab should, of course, also be thick enough to give a proper description of the surface and near surface relaxations.

The calculated surface core level shifts as a function of slab thickness are shown in Fig. 2(a) for the bare Pd(111) surface together with the shifts with adsorbed H and O, respectively. For the bare surface, a five layer slab is sufficient to reach a convergence in the SCLS within 50 meV.

When considering the convergence for SCLS in the case of adsorbates, it is important that the bulk reference does not change upon the adsorption. In order to investigate this, we have calculated the CLS for the bare surface in the presence of an adsorbate on the opposite side of the slab. The results [Pd(back)] in the case of hydrogen and oxygen are shown in Fig. 2(a). For hydrogen, the results are close to the case without adsorbates, which indicates that a five layer slab is sufficient for a convergence within 50 meV. The situation is different for oxygen. It is only for 9 and 11 layers that a CLS is calculated that coincides with the one without adsorbates. The reason for the deviation is revealed by investigating the adsorbate induced polarization of the