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First principles study of the binding energies of pure metals using FP-LAPW method

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ABSTRACT

It is known that ionization potentials can be calculated in density-functional theory using Slater transition state technique. In this work a modified version of this technique is used to calculate binding energies for 31 metals. The technique to produce these energies involves ab-initio calculations performed using the FP-LAPW method, with the GGA approximation using the DFT formalism according to the implementation in the Wien2k code.

In these calculations the occupation of the 1s states was reduced according to the fractional core hole as a function of *Z*, which is presented in this work. The theoretical *K*, L_1, L_2 and L_3 binding energies were compared with Berkeley ionization energies and they show a considerable improvement compared to those calculated with the normal occupation of the 1s state.

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1. Introduction

A persistent problem in the local-density theory of electronic structure is that the eigenvalues of the one-electron Schrödinger equations do not give a good representation of the electron binding energies. Total energies of atoms, molecules, and solids are ordinarily quite accurate, but when electrons are removed or shifted from one level to another the eigenvalues do not by themselves give an accurate account of the change in energy. For this reason the objective of Slater transition state technique [1] is the accurate evaluation of electronic excitation energies of finite molecular systems.

Slater has studied the role of eigenvalues in representing excited-state energies in atoms and molecules and found that self-consistent field calculations for a nonphysical state halfway between the ground state and an excited state were useful in calculating excitation energies [2].

The transition state technique according to Slater considers the removal of charge associated with half an electron of the state of study [3–7]. In this technique the hole is confined to one cell of the solid's lattice.

We used Slater's idea but instead of the half electron core hole we propose an optimal fractional core hole (fch) to obtain binding energies. We apply the fch to ab-initio calculations performed in pure metals using the full potential linearized augmented plane-wave (FP-LAPW) method implemented in Wien2k code.

We improved the calculated binding energies by changing the occupation of the 1s state and adding the removed electron fraction to the uniform background charge. With this procedure we obtained an optimized fractional core hole (fch). The results for 1s, 2s and 2p binding energies are in good agreement with the ionization energies tabulated in the X-ray Data Booklet (XrDB) of Lawrence Berkeley National Laboratory (LBNL) [8].

The periodic boundary conditions create artificial interactions between core holes in neighboring unit cells. In order to reduce these interactions it is convenient to enlarge the distances between core holes using supercells.

We tested if supercell calculations were necessary for metals by comparing the results obtained with supercell and single cell calculations. As both results were nearly identical we use single cells in order to reduce the calculation time.

The paper is organized as follows. In Section 2 we describe how we implement the transition state concept in our calculations and how we obtain the optimized fractional core hole. In Section 3 we present the computational details of our calculations. In Section 4 we investigate if supercell calculations are necessary for metals. In Section 5 we present the results obtained for 31 metals after combining our perspective of Slater transition state technique and the self-consistent calculations. In Section 6 we present the conclusions of this work.

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2. The model

Slater transition-state scheme assumes that the variation of total energy with respect to the occupation number is expandable in a Taylor series. It therefore allows for the existence of fractional occupation numbers [9]. Slater pointed out that a better physical picture in insulators and semiconductors is a localized hole [4]. This idea has been implemented by specifying a simple model for the hole: it is confined to one cell of the solid's lattice.

Liberman [2] says that the final assumption in the transition-state model is that the orbital functions, from which the charge density is constructed, are Bloch functions and have the appropriate boundary conditions so that a standard band-structure method may be used for the calculation.

We applied the technique to metals, assuming that the energies of interest correspond to the deepest levels, belonging to core states.

The theoretical eigenvalues are related to the binding energies by:

$$E_{\text{binding},i}\,[\text{eV}] = (\epsilon_{\text{f}} - \epsilon_{\text{j}})$$

for $i = K, L_1, L_2, L_3$ and where ϵ_{f} is the Fermi energy, ϵ_{j} is the eigenvalue produced by the self-consistent calculation for state j, j being 1s, 2s, 2p, 2p* respectively, and p and p* address for $\text{p}_{1/2}$ and $\text{p}_{3/2}$ states respectively.

We introduced a partial occupation number as a fractional core hole (fch) at the 1s state of the atom which hosts the core hole. In doing so we could vary between no electron missing and one electron missing. This allowed us to optimize the calculated 1s binding energy according to the ionization energies tabulated in the X-ray Data Booklet [8].

The fractional core hole was implemented in the Wien2k calculation by changing the occupation of the corresponding core 1s state of one of the atoms and adding the same electronic fraction to the uniform background charge.

This fractional core hole was applied to the transition and simple metals we wanted to study.

Wien2k calculations showed that the binding energies obtained without core hole (normal occupation) were smaller than the tabulated binding energies. With a half electron core hole as was suggested by Slater the energies obtained were too big. Still a fractional core hole of 20% of an electron produced energies larger than the tabulated ones in most cases and smaller in a few cases. The energy results didn't agree well with the tabulated values [8] when a fixed fractional core hole was used in all the metals.

The method we propose to optimize the fractional core hole consists first in calculating the *K* binding energies of the 1s state for each *Z* for the two known cases: without core hole (0%) and with a fractional core hole of 20% of an electron. Assuming a linear behavior of the energy versus the fractional core hole, we could interpolate the value that reproduces the tabulated energy for that *Z*. Once we had the fractional core holes that reproduce the ionization energies [8] as a function of *Z* we could fit a polynomial function for the fractional core hole (fch), see Fig. 1. In our fit Zn ($Z = 30$) was not included, because the value did not follow the trend of the other metals.

These were the fractional core holes finally used in the calculations that we show in the rest of the paper.

For the calculation of the *L* binding energies we did no further adjustment of the fractional core hole.

3. Theoretical method

Self-consistent calculations of total energies and the electronic structure based on the scalar relativistic full-potential linearized augmented plane-wave and local orbitals method (FP-LAPW+lo) were carried out using the Wien2k 12.1 package [10-12]. This is one of the most accurate schemes to solve the Kohn–Sham equations of DFT in which exchange and correlation effects are treated, for example, by the generalized gradient approximation (GGA), which often leads to better energies and equilibrium structures than LDA [13,14]. In this paper we used the Perdew, Burke and Ernzerhof (PBE) functional which has been the standard GGA functional for solid-state calculations until now. The equilibrium lattice parameters we obtained were very similar to those presented by Haas et al. [15] using PBE approximation.

The required precision in total energy was achieved by using a large plane-wave cutoff of $RK_{\text{max}} = 10$ (resulting in more than 300 plane-waves) and a k-point sampling in the Brillouin zone (BZ) of about 5000 points. This corresponds to 250 k points in the irreducible wedge. For each of the elements the full analysis was carried out at the theoretical equilibrium volume.

4. The supercells

The artificial interactions between neighboring core holes created by the periodic boundary conditions can be reduced by enlarging the distances between them. In order to reduce these unwanted interactions we performed supercell calculations.

In the $2 \times 2 \times 2$ cell, created to perform supercell calculations, only one atom had a fractional occupation in the 1s state and for the remaining atoms the core occupancy was left unchanged.

For the sake of comparison we performed the supercell and single cell calculations for several metals. We show the results for Au,

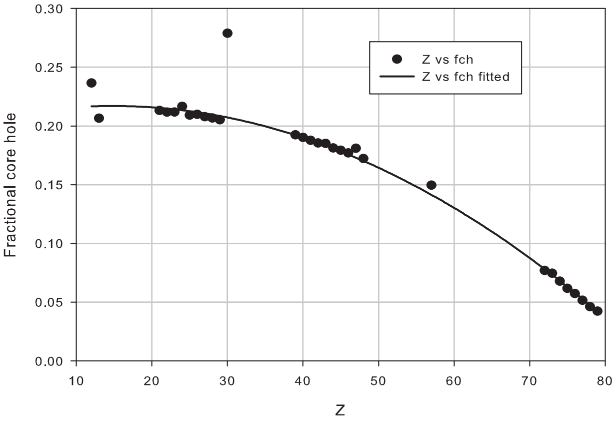

Fig. 1. Fractional core hole (fch) of the 1s state as a function of *Z*. The fitted polynomial function of second degree is $\text{fch}(Z) = a + b * Z + c * Z^2$, $a = 20.7677$, $b = 0.1258$ and $c = -4.2446\text{E}{-3}$.

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