

Analysis of electronic structure and X-ray Absorption and Emission spectra in MgO within the FP-LAPW method

Resumen

In this work we calculated *ab initio* X-ray Absorption and Emission spectra using the Full Potential Linearised Augmented Plane Wave method within the Density Functional Theory formalism in MgO.

The X-ray absorption and emission spectra for the K and $L_{2,3}$ edges of Mg and O atoms were calculated including the core hole in order to study the electronic structure of valence and conduction band of the system. Both kinds of spectra were compared with experimental data obtaining a very good agreement and the improvement in the spectra due to the use of Tran Blaha modified Becke-Johnson potential is manifested.

The Bader's topological method was employed to analyse the ionic behaviour. The charge density for MgO and a Wannier function for O are also shown.

keyword: core hole, K and $L_{2,3}$ edges, ab-initio calculations, XANES, XES.

1. Introduction

X-ray Absorption Near Edge Structures and Emission spectroscopy (XANES and XES) are among the most important tools for the characterization of the electronic structure of the materials through the analysis the densities of states, the valence and conduction bands and the optical properties. Several experimental [1, 2] and theoretical calculations using different approaches [3, 4] carried out XANES and XES studies.

In the *ab initio* methods the local-density approximation (LDA) [5] or the generalized gradient approximation (GGA) usually are good choices, but fail when calculating semiconductor densities of states [6]. A modified Becke-Johnson exchange potential was tested by Tran and Blaha for the calculation of band gaps giving much better results [7, 8].

In this work we performed X-ray spectra using all electron calculations within the density functional theory (DFT) formalism [9], with different potentials: Perdew-Burke-Ernzerhof (PBE) [6], local density approximation plus Hubbard U parameter (LDA+U) [10] and Tran Blaha modified Becke-Johnson

(TB-mBJ) [11]. The results were compared against the experimental spectra, analysing the partial contributions of the densities of states for the K and L edges of MgO including the core hole technique.

The hole left by the excited core electron changes the electronic structure of the crystal, to consider this effect we performed the spectra with fractional core holes within the Slater [12] approximation, using supercell calculations.

2. Theoretical method

The *ab initio* calculations were carried out using the WIEN2k 16 package [9, 13], which uses all electron self-consistent calculations based on the scalar relativistic full-potential linearised augmented plane-wave basis set combined with local orbitals (FP-LAPW+lo). This is one of the most accurate schemes to solve the Kohn-Sham equations of density functional theory [5, 14]. The LDA and GGA functionals usually yield ground-state properties, which are in reasonable agreement with the experiments. However, this sometimes is not the case for excited-state properties.

Methods that retain the computational efficiency of standard DFT but improve the spectroscopic properties are potentially of great interest, consequently improvement has been achieved by LDA+U and a modified version (TB-mBJ) [8, 11] of the Becke and Johnson (BJ) exchange potential [7]. The TB-mBJ calculations are produced using PBE or LDA converged calculations as starting point.

We can calculate near edge structure of X-ray absorption and emission spectra according to the formalism described by Schwarz *et al.* [15] for the dipole allowed transitions.

The transition state technique according to Slater considers the removal of charge associated with half an electron of the state of study [12], to calculate excitation energies. Instead we use fractional core holes to find the optimal match with the experiments. The calculations were produced with core holes 0.0, 0.5 and 1.0 for the K lines and the one that shows the best agreement with the experiment was compared with the partial densities of states that contributes to the edge.

The XANES and XES spectra were calculated for K and L lines and they were convoluted with a Lorentzian to account for lifetime broadening and resolution of the spectrometer. The required precision in total energy was achieved by using a large plane-wave cutoff of

$RK_{\max} = 8$, (where R is the muffin-tin radii and $K_{\max}$ is the cutoff in the plane wave expansion of wave functional), resulting in a kpoint sampling in the Brillouin zone (BZ) of about 500 points.

The analysis was carried out at the theoretical equilibrium volume based on PBE and LDA+U calculations.

3. Results and discussion

In this work we performed *ab initio* calculations in order to analyse the electronic properties, DOS, XANES and XES spectra for the different edges of MgO. The MgO cubic structure was optimized and the lattice parameter obtained self-consistently using PBE and LDA+U calculations are 4.261 Å and 4.315 Å respectively, which are larger than the experimental MgO lattice parameter 4.186 Å. The PBE calculations give better lattice parameter than the LDA+U compared to the experiments and this result is exactly the same as the one obtained by Haas *et al.* [16].

The band gap obtained with the PBE calculation is 4.42 eV, the band gap obtained with LDA+U is 4.05 eV, the difference was made by the TB-mBJ calculation giving 7.16 eV which compares much better than the others with the experimental one 7.83 eV [8].

3.1. X-ray Absorption Spectroscopy

We considered transitions from the $1s$ (K edge) and $2p$ ($L_{2,3}$ edge) core levels of Mg atom and from the $1s$ (K edge) core level of O atom to the conduction band. We calculated PBE and TB-mBJ XANES spectra including the fractional core hole technique and compared with the experimental data [1, 2] to obtain the best match, which was obtained with the full core hole.

In Figures 1 and 2 we show the calculated Mg $L_{2,3}$ spectra using PBE and TB-mBJ with full core hole compared with the experimental spectrum [2]. The first peak in the XANES experimental spectrum just above the energy gap, around 8 eV is smaller using PBE than TB-mBJ. For the higher energies, the spectrum using TB-mBJ shows better agreement with the experimental spectrum.

In Figures 3 and 4 we show the O K and Mg K spectra calculated using TB-mBJ and full core hole, compared with the corresponding experimental spectra and the corresponding p DOS states. We show TB-mBJ calculations as they have better agreement with the experimental spectra [1, 2] compared to PBE calculations.

We observed, as was described for other semiconductor systems [17, 18], the MgO XANES spectra using the TB-mBJ potential and a full core hole show the best agreement with the experiments and provides a better description of the excited states.

3.2. X-ray Emission Spectroscopy

We also analyzed XES transitions from the valence band to the $1s$ (K edge) and $2p$ (L edge) levels of the Mg atom and from the valence band to the $1s$ (K edge) for O atom.

In Figures 5 and 6 we show the O K and Mg K calculated spectra using TB-mBJ compared with the corresponding experiments shown in references [19, 20] and the corresponding p -projected DOS states. The Mg $L_{2,3}$ spectrum using TB-mBJ is shown in Figure 8 compared with the experimental spectrum obtained from references [20, 21, 22, 23].

The emission spectra are shown with the corresponding projected valence DOS states, p for K edge and s and d for Mg $L_{2,3}$ edges. These DOS peaks below Fermi energy are mainly from O $2p$ states hybridized with Mg $3s$ and $3p$ states. The best agreement with the experiment is obtained without core hole in PBE and TB-mBJ, this makes sense as the XES final state has no core hole, the TB-mBJ potential shows a better agreement in the lower energy region.

In the unbroadened Mg $L_{2,3}$ spectrum the s contribution is bigger than the d contribution, the same trend is observed in the DOS plot. The broadened spectrum inverts the relationship between these peaks in agreement with the experiment in both, PBE and TB-mBJ calculated spectra.

There is a small d contribution in the density of states below the Fermi energy identified as well in the XES Mg $L_{2,3}$ spectrum, on the contrary in reference [22] the authors deny this presence. However, it is expected that under compression, d bands move down in energy, so the number of d states below the Fermi energy increases. In MgO the d states effect is more important due to the bonding with the oxygen, than in metallic Mg, where d contribution is almost negligible in the valence band for the equilibrium Mg volume, compared to the s and p contributions.

To show this effect is more important when the volume cell decreases and the oxygen atom is closer to the magnesium atom, we performed calculations for different volumes showing the evolution of d -projected states under compression of the unit cell. In Figure 9 the d states contribution is almost negligible for the 100 percent of growth of the cell. Moreover, the shift in energy of the d states to lower energies is observed when the volume cell decreases.

In the experimental Mg XES $L_{2,3}$ spectrum there is an extra peak which is not observed in the calculated spectrum. We calculated the transitions corresponding to the Mg $L_{2,3}$ contributions and we include the intrashell $2p \rightarrow 2s$ transition as well, shown in Figure 10. Our plot was produced with the numerical convolution between $3s$ and $3d$ states with $2p$ states, the same procedure was applied to the $2p \rightarrow 2s$

transition, as they are states that belong to the same $n = 2$ level we call them intrashell transitions. This extra transition corresponds to the same energy as the extra experimental peak observed. This scheme was performed assuming a plain transition matrix, so the intensity should not be considered. It could have been produced in the experiment by an unwanted excitation of the $2s$ level and filled again by a transition $2p \rightarrow 2s$, present in a very small proportion.

Our X-ray Mg $L_{2,3}$ emission spectrum agrees better with the XPS shown by King *et al.* [22] than with the experiment in references [20, 21] because XPS does not get the extra peak, this confirms it does not belong to the Mg $L_{2,3}$ edge, and should be an artefact of the measurement.

3.3. Charge density

In order to visualize the chemical bonding directly we present the valence-charge densities. In Figure 11(a) the (110) plane of the charge density is plotted, Mg atoms on the corners have less charge, and the O atoms concentrate most of the electronic charge density. In Figure 11(b) we show the maximally localized Wannier functions (MLWF) for the p states of O in MgO calculated using Wannier90 according to the Marzari and Vanderbilt *et al.* method [24].

Bader's method was applied to determine the charge transfer from Mg to O. We obtained the total charge of Mg and O atoms using the AIM program produced by J. Fuhr which analysis the topology of the charge density according to Bader's method Atoms in Molecules (AIM) [25]. After the self consistent calculation AIM provides the volume that belongs to each atom and integrates the charge in that volume: Mg volume is 31.279 a.u. and the total electronic charge is 10.276 electrons, which indicates a loss of 1.724 electrons, compared to the free Mg atom. O volume is 99.159 a.u. and the total electronic charge is 9.724 electrons, which indicates a gain of 1.724 electrons, compared to the free O atom, meaning Mg transferred 1.724 electrons to the O atom, which is consistent with expected trends in ionicity.

Using the electronic charges obtained with the Bader's topological Method, the Coulomb potential and the Madelung constant of 1.74756 we obtained the Lattice Energy 3377 kJ/mol for the equilibrium lattice parameter and 3429 kJ/mol for the experimental lattice parameter, we compared them with the 3890 kJ/mol value obtained by the Born-Haber cycle. The value we obtained is smaller than the Born-Haber cycle because that one corresponds to a transferred charge of 2 electrons against the 1.724 we discussed previously.

The O distribution of charge is more extended than Mg distribution according to Bader, this is consistent with the charge density plot in Figure 11 (a) where the O atom concentrates most of the electronic charge and the p character of the O orbital is shown in Figure 11 (b) by the oxygen Wannier function.

4. Conclusion

In this work MgO X-ray absorption near-edge spectra and X-ray emission spectra spectra were calculated using different potentials (PBE) Perdew-Burke-Ernzerhof (PBE) [6], local density approximation plus Hubbard U parameter (LDA+U) [10] and Tran Blaha modified Becke-Johnson (TB-mBJ) [8] and compared with experimental results [1, 2, 19, 20, 21, 22].

The experiments were better reproduced by introducing the full core hole in the calculations using TB-mBJ potential. Furthermore, our X-ray Mg $L_{2,3}$ absorption spectra calculated using TB-mBJ potential and full core hole compares better with the experiment than the one calculated by Olovsson *et al.* [4] using the BSE formulation. BSE theory though it is a better approximation, is not needed in this case. The TB-mBJ is worth using as this functional describes better the semiconductors, produces a band gap that is similar to the experimental value and improves the structure of the spectra.

The DFT is formally a theory for the ground state, nevertheless it gives a good estimate in properties that involve excited energy states like absorption or emission spectra [15].

Our XES calculations were compared with experimental results for Mg K and $L_{2,3}$ XES spectra [21, 23, 26] and O K [19]. The best agreement was obtained without core hole. The calculated XES spectra reproduce the main features of the experimental spectra for the Mg K , O K and Mg $L_{2,3}$ edges.

There is a small experimental peak not reproduced by the calculated Mg $L_{2,3}$ XES spectrum because this only reflects the transition from valence states to $2p$ states. This peak could have been produced by an undesired excitation of the $2s$ states. We consider that finding these intrashell transitions in Mg atom is relevant, as is normally expected in bigger atoms like Uranium [27].

The intensities relationship of the $3s$ and $3d$ contributions in Mg $L_{2,3}$ spectrum is improved respect to the PBE potential and the low energy peaks are better reproduced. In the experimental spectrum the s contribution is smaller than d , the same behaviour is shown using the proper broadening parameter in both PBE and TB-mBJ calculated spectra. This behaviour shows that the TB-mBJ potential not only corrects the band gap but also improves the intensities of the peaks as well. We show the presence of Mg d states under the Fermi energy in the equilibrium volume of MgO.

We obtained the total charge of Mg and O atoms in the MgO equilibrium unit cell after the calculation is converged, this shows that a very important part of the $3s$ electronic charge of the Mg atoms has been transferred to the O atom in agreement with the ionic behaviour of MgO. Our value of the Lattice Energy is comparable in order of magnitude with the empirical Born-Haber cycle value.

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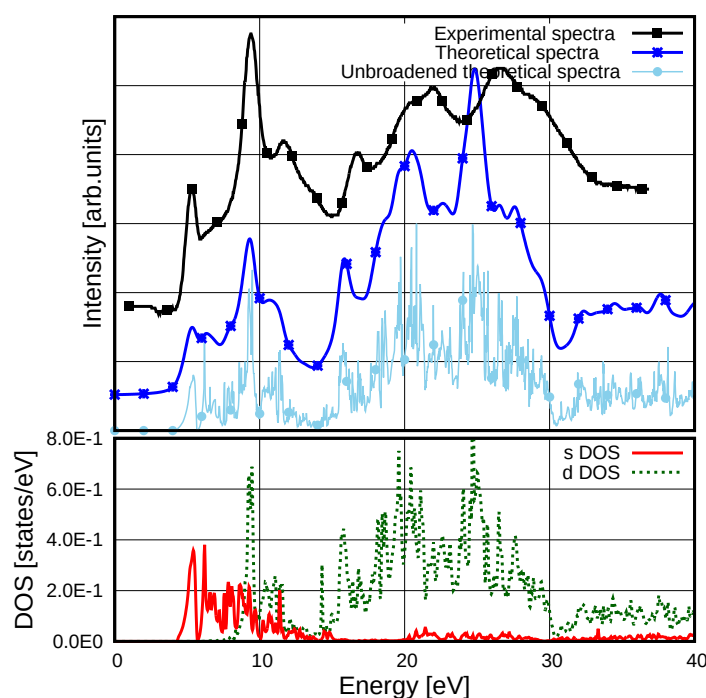


Figure 1: Mg XANES $L_{2,3}$ edges spectrum calculated using PBE with full core hole compared with the experimental one and the s , d -projected DOS.

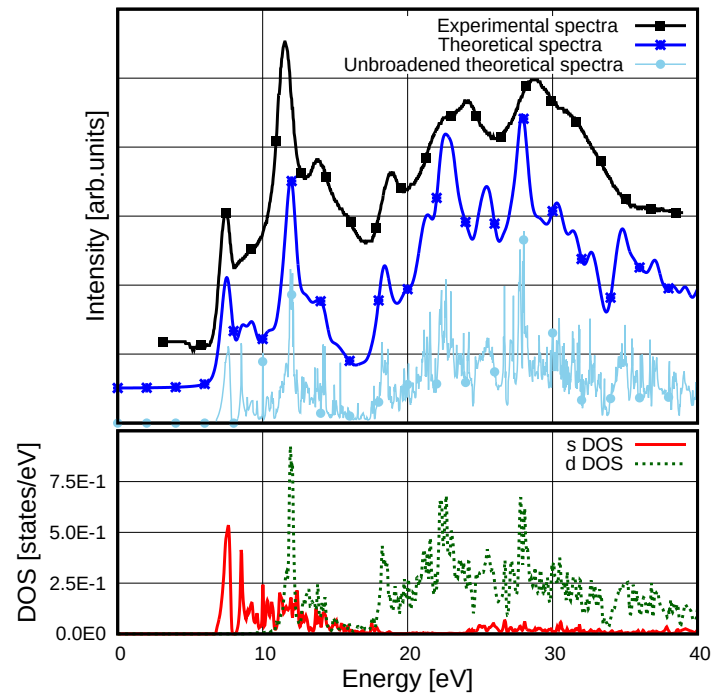


Figure 2: Mg XANES $L_{2,3}$ edges spectrum calculated using TB-mBJ potential with full core hole compared with the experimental one and the s , d -projected DOS .

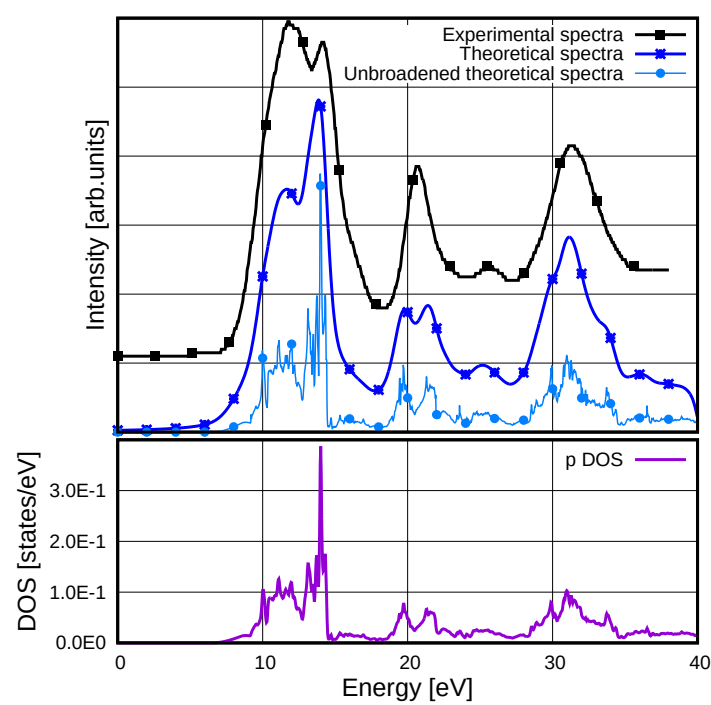


Figure 3: O XANES K edge spectrum calculated using TB-mBJ potential with full core hole compared with the experimental one and the p -projected DOS.

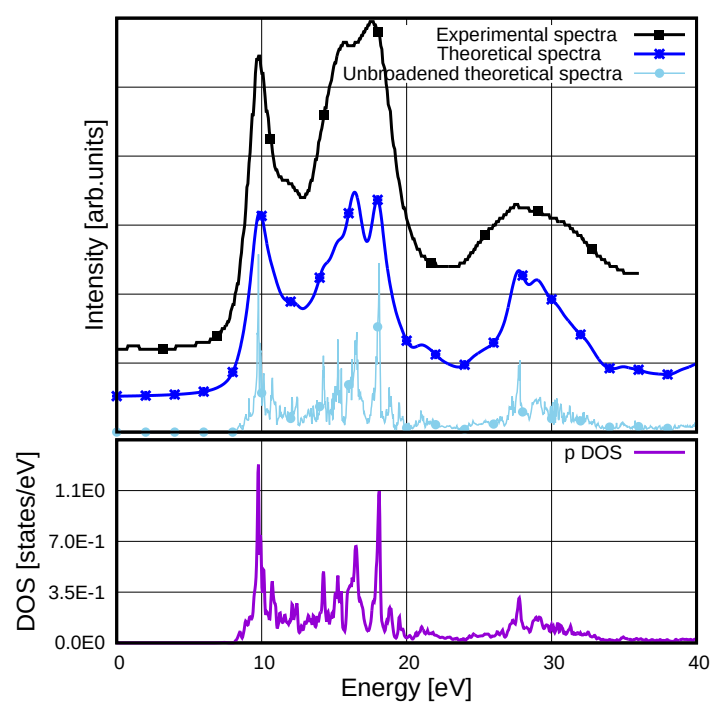


Figure 4: Mg XANES K edge spectrum calculated using TB-mBJ potential with full core hole compared with the experimental one and the p -projected DOS.

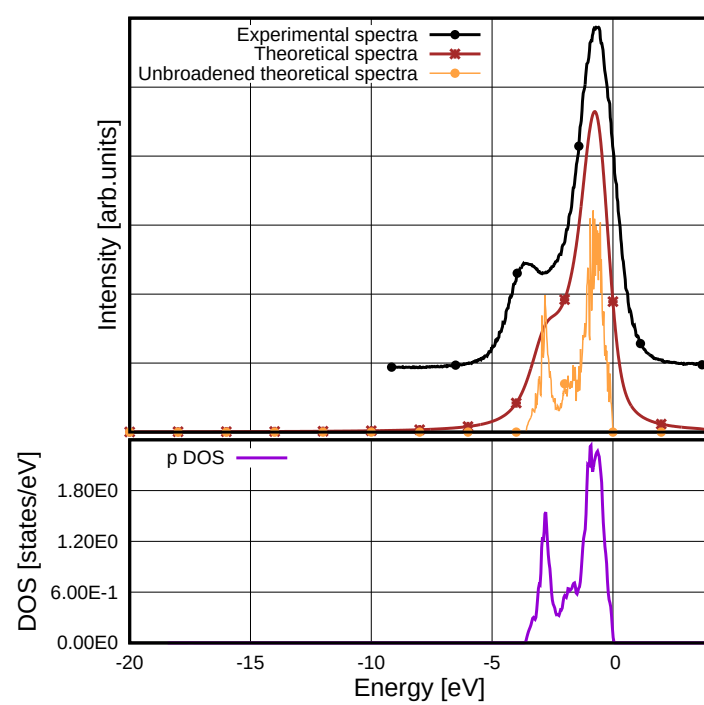


Figure 5: O K XES spectrum compared to p -projected DOS calculated using TB-mBJ potential without core hole in MgO.

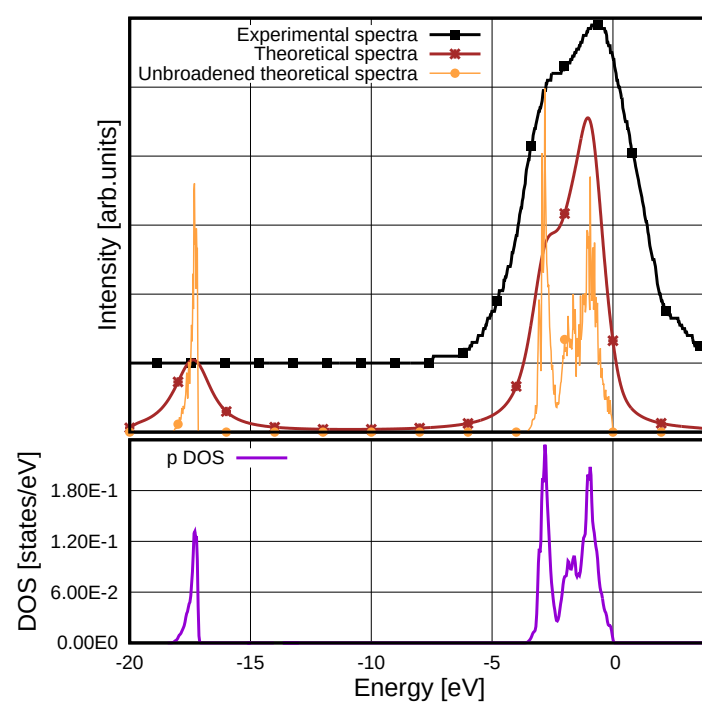


Figure 6: Mg K XES spectrum compared to s and d -projected DOS calculated using TB-mBJ potential without core hole in MgO.

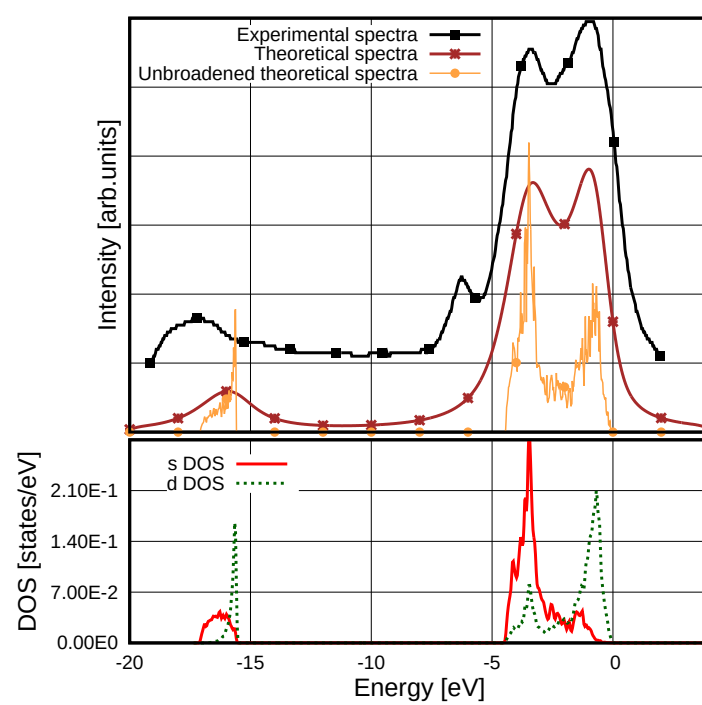


Figure 7: Mg $L_{2,3}$ XES spectrum compared to s and d -projected DOS calculated using PBE potential without core hole in MgO.

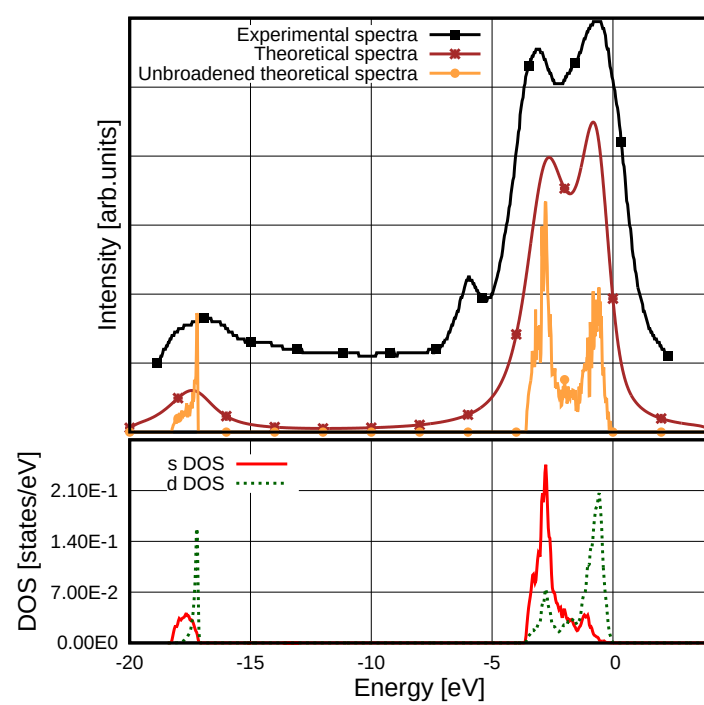


Figure 8: Mg $L_{2,3}$ XES spectrum compared to s and d -projected DOS calculated using TB-mBJ potential without core hole in MgO.

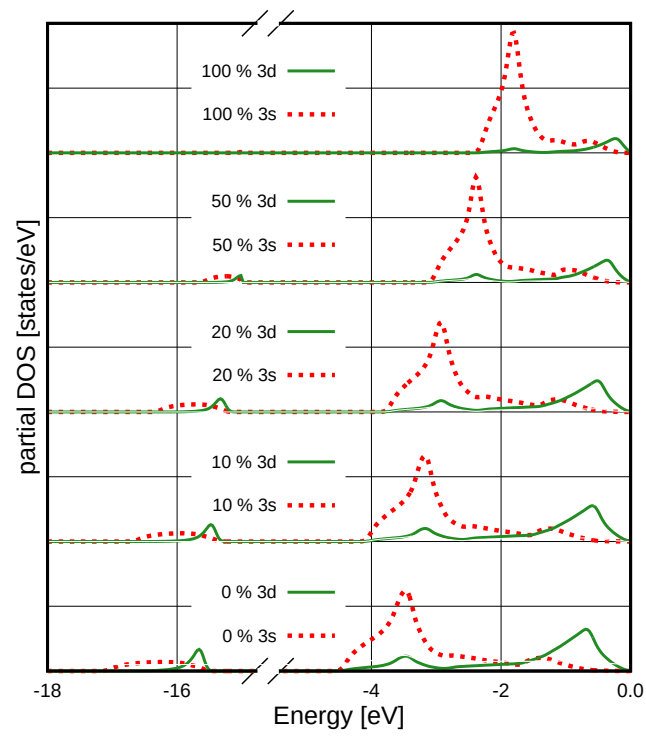


Figure 9: *s* and *d* projected DOS contributions as a function of the volume

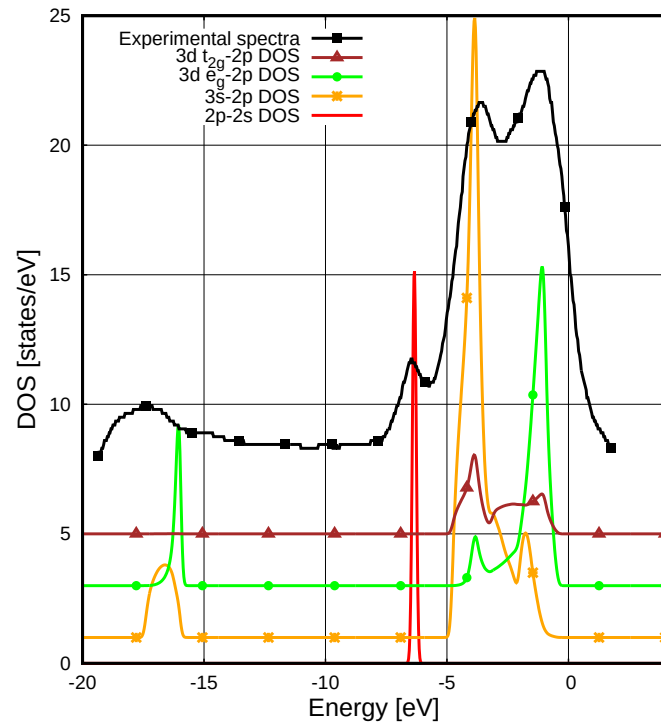


Figure 10: XES Mg $L_{2,3}$ spectrum plus $2p \rightarrow 2s$ extra peak

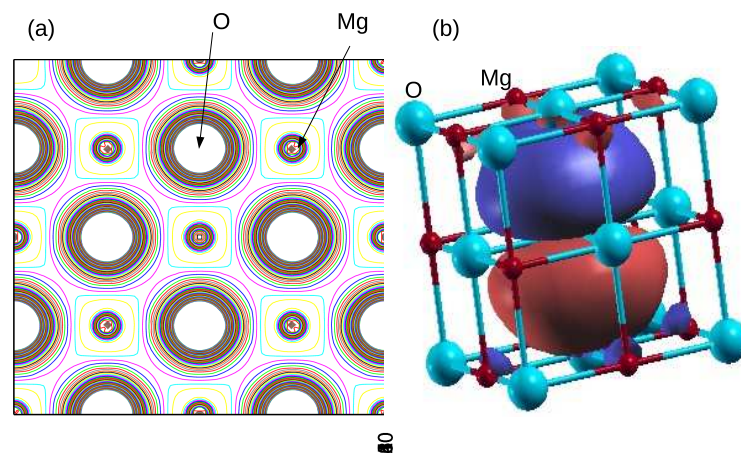


Figure 11: Electronic charge density plot on the (110) plane (a) and the oxygen Wannier function (b).