Combined first principles and many-body theory modelling of x-ray absorption spectra of bulk MgO and $SrTiO_3$

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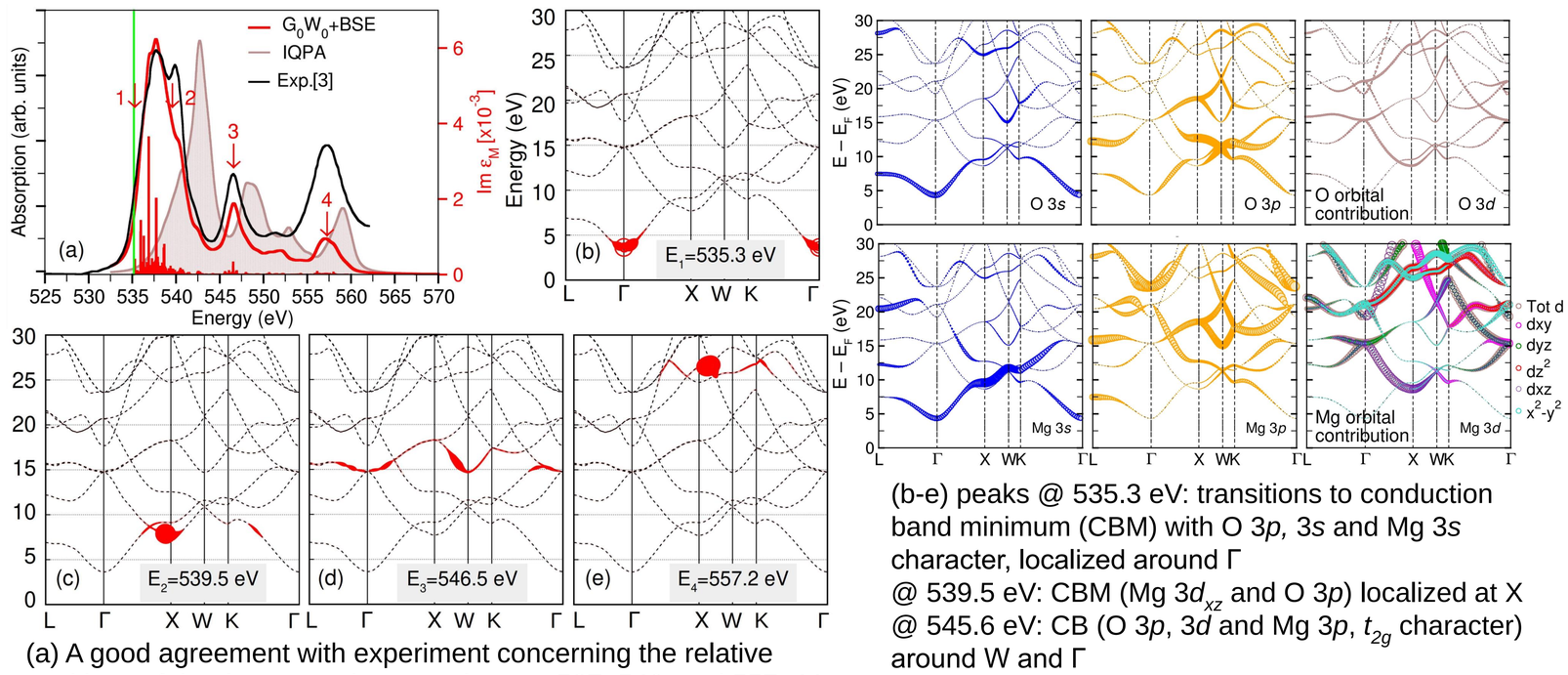
Abstract

We present a comprehensive study of the x-ray absorption spectra (XAS) in two paradigmatic oxides − MgO and $SrTiO_3$, from first-principles calculations. The spectra are calculated by including the quasiparticle corrections with G_0W_0 (MgO) / within the independent particle approximation ($SrTiO_3$), followed by the excitonic effects by solving the Bethe-Salpeter Equation (BSE). Our results show that inclusion of the electron-(core)hole interactions with BSE is integral to describe the spectra accurately. The simulated XAS spectra for the O K edge in MgO [1], and in $SrTiO_3$ [2] are in excellent agreement with experiment w.r.t. the spectral shape and peak positions. The theoretical Ti-$L_{2,3}$ edge[2] is concurrent with experiment w.r.t. the energetic positions of the four-peak structure stemming from the crystal-field splitting due to the Ti octahedral coordination in $SrTiO_3$. We also analyze the origin of prominent peaks and identify the orbital character of the relevant contributions by projecting the e-h coupling coefficients from the BSE eigenvectors on the band structure. The real-space projection of the wave functions for the lowest energy exciton of the O K-edge shows a strong localization (MgO), whereas a two-dimensional spread in the *x-y* plane is observed for $SrTiO_3$.

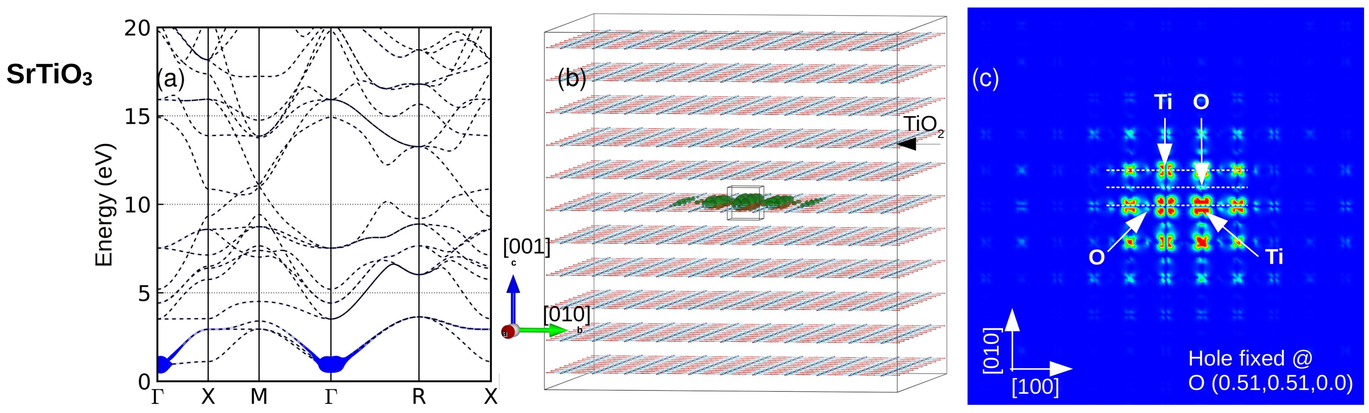
O K edge in MgO[1]



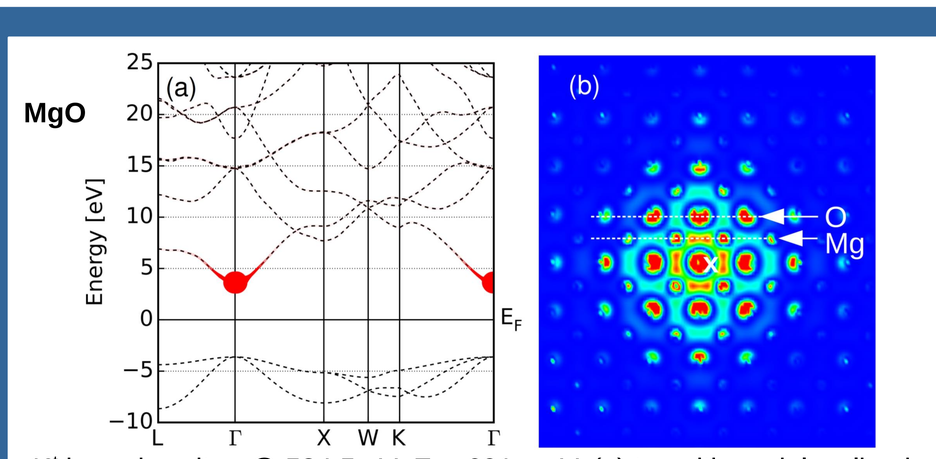
(a) A good agreement with experiment concerning the relative positions of the three prominent peaks at ~ 537, 546, and 557 eV is obtained only after the G_0W_0+BSE corrections,

(b-e) peaks @ 535.3 eV: transitions to conduction band minimum (CBM) with O 3*p,* 3*s* and Mg 3*s* character, localized around Γ
@ 539.5 eV: CBM (Mg $3d_{xz}$ and O 3*p*) localized at X
@ 545.6 eV: CB (O 3*p*, 3*d* and Mg 3*p*, t_{2g} character) around W and Γ
@ 557.2 eV: CB with energies > 25 eV (O 3*p* and Mg 3*p*, e_g) along X − W − K − Γ.

Real-space analysis of 1st bound exciton: O K edge in $SrTiO_3$[2] and MgO[1]

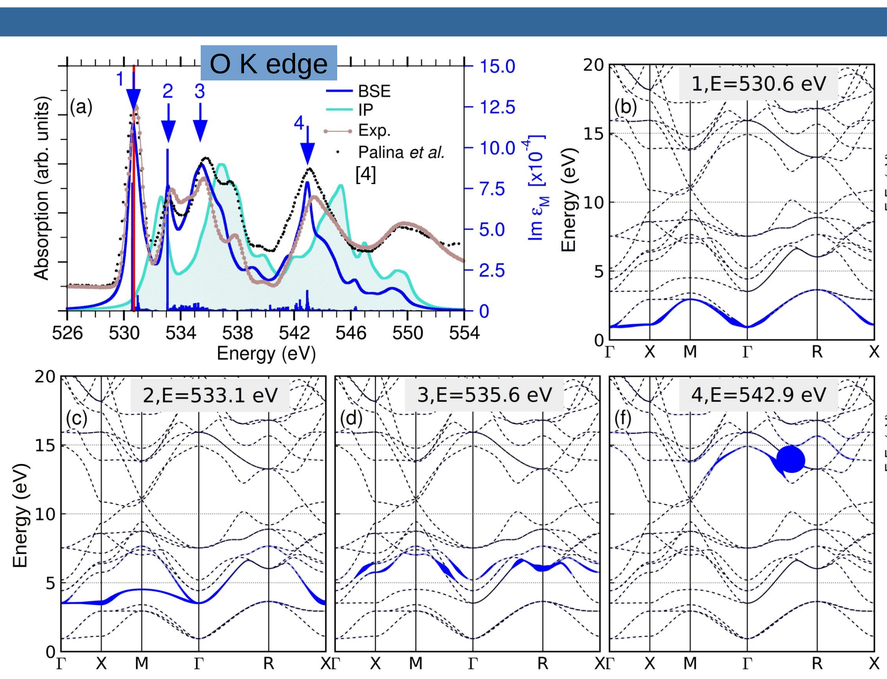


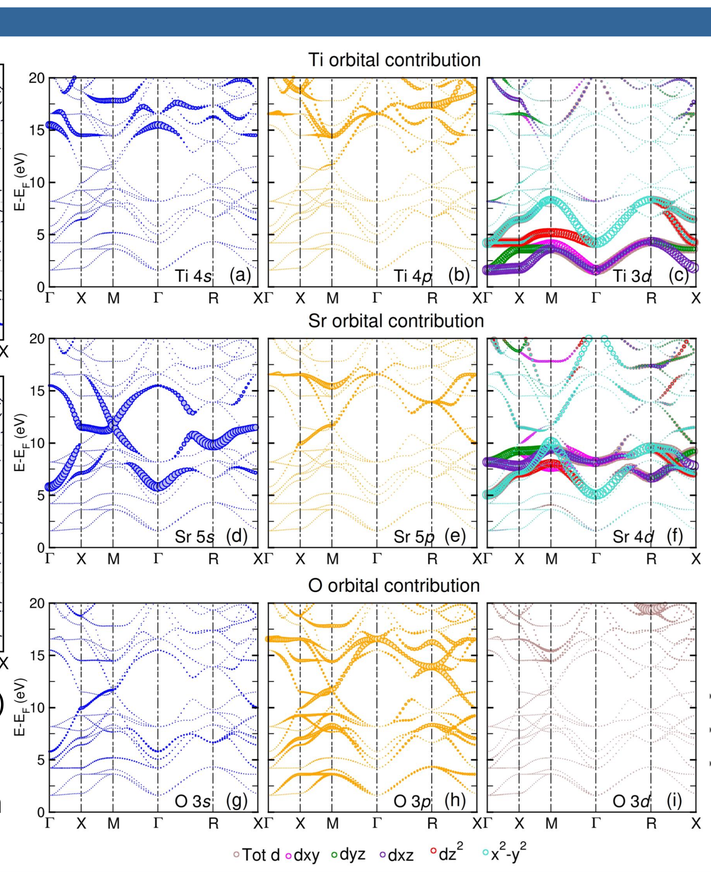
1st bound exciton @ 503.73 eV, E_B= 468 meV, (a) transitions to CBM, delocalized along Γ − X, M − Γ − R, (b and c) excitonic wave function spreads up to three unit cells with distinct two-dimensional character and maximum intensity near Ti-sites, and hybridization of the Ti t_{2g} and O *p* states.

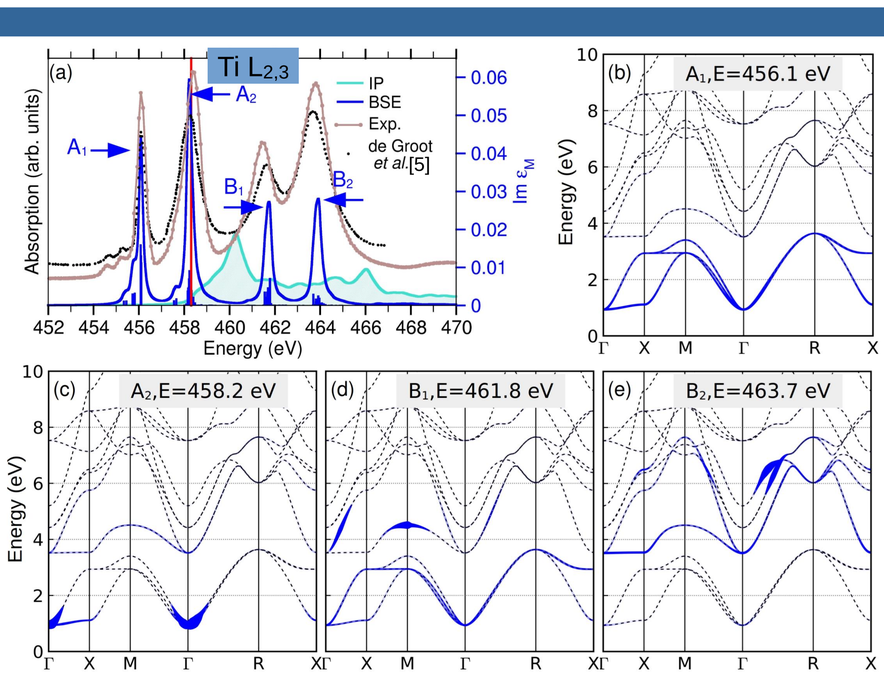


1st bound exciton @ 534.5 eV, E_B= 691 meV, (a) transitions delocalized along L − Γ − X and K − Γ, (b) the spread is confined to two-three unit cells with *s* and *p* character near O sites and *s*-like near Mg sites

O K edge and Ti $L_{2,3}$ edge in $SrTiO_3$[2]







- (a) Calculated O K-edge obtained by including excitonic effects (BSE)
- (b-e) peaks @ 530.6 eV: transitions to CBM (Ti t_{2g} character)
- @ 533.1 eV, 535.6.1 eV: CB (Ti e_g character) where the peaks have dispersive contributions along the whole **k**-path, @ 542.9 eV: CB with energies >12 eV, Sr 5*s* hybridized with Sr 5*p* and Sr d_{x2-y2} character

(a) Calculated Ti $L_{2,3}$ edge obtained by solving BSE,
(b-e) peaks @ 456.1 eV: transitions to CBM (Ti t_{2g} character),
@ 458.2 eV: CB with predominantly Ti e_g characer localized around Γ,
@ 461.8 eV: CB with Ti t_{2g} and e_g character, dispersive contributions throughout the **k**-path, @ 516.4 eV: CB with Ti d_{z2} character.

Method

Electronic properties:
Exchange-correlation functional- PBEsol

XAS spectrum:

- Independent particle approximation
- Many-body effects within *GW* (single-shot G_0W_0) and BSE

Codes: VASP, exciting (Nitrogen) and Wannier90

References

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