Relativistic Effects in Heavy-Element Oxides: A Comparative DFT Study of MoO_3, WO_3, and ThO_2

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Relativistic effects were investigated for MoO_3, WO_3, and ThO_2 using density functional theory with scalar-relativistic and spin–orbit-coupled pseudopotentials to quantify how spin–orbit coupling influences total energies, band structures, and projected densities of states across increasing atomic number. The results show that spin–orbit coupling provides only minor corrections for MoO_3 and moderate band splittings for WO_3, but induces large energy shifts and strong band and peak splittings in ThO_2, demonstrating that relativistic effects become essential for accurately describing heavy-element oxides.

I. INTRODUCTION

A. Background

The main method with which one can model quantum-chemical properties of materials is the Density Functional Theory. However, the standard non-relativistic Schrödinger equation becomes insufficient when describing systems with heavy elements. As the atomic number Z increases, the strong nuclear potential forces the speeds of core electrons to approach the speed of light. This introduces relativistic effects, which fundamentally alter the energy terms of the electronic Hamiltonian, leading to contraction of s and p orbitals and the expansion of d and f orbitals.

In computational practice, these effects are incorporated through specific pseudopotentials (PPs), generally categorized into two types: Scalar-Relativistic (SR) and Spin-Orbit Coupled (SOC). SR PPs account for the mass-velocity correction - the relativistic mass increase - and the Darwin term - smearing of the electron charge - while averaging out the spin-dependence. This fails to capture the interaction between an electron's intrinsic spin and its orbital angular momentum. The Spin-Orbit Coupling is responsible for splitting electronic orbitals into sub-orbitals characterised by total angular momentum j. These corrections scale at approximately Z^4, which means that while being negligible for light elements, they become increasingly important for heavy elements like Thorium.

Neglecting SOC in heavy elements leads to rather large inaccuracies when it comes to predicting the properties of materials. Some of these parameters include band structures, band gaps, density of state plots, etc. Additionally, the description of optical spectra (when working with molecular codes) becomes incorrect when relativistic effects are neglected. This project investigates the importance of SOC by comparing a number of specific properties calculated for MoO_3, WO_3, and ThO_2.

II. COMPUTATIONAL PARAMETERS UTILISED

A. DFT Setup, Convergence Criteria

The calculations were performed using Quantum ESPRESSO software, with PBE functionals used for all calculations. Each calculation was performed twice, once with the SR PP and once with the SOC PP. All PPs were generated using atomic code by A. Dal Corso, and all were of the PAW type.
The choice behind the convergence criteria represented a compromise between the precision of the calculation and the computational difficulty that the choice of the said parameters represented. The three main parameters for which the convergence tests were made were: ecutwfc (kinetic energy cutoff for wavefunctions), ecutrho (kinetic energy cutoff for charge density) and k-points. The final values for these parameters are summarised in the table below. While the values for the k-points might seem low, their further increase did not bring a meaningful improvement in the results.

TABLE I: Converged parameters used during calculations

	MoO_3	o-WO_3	m-WO_3	h-WO_3	ThO_2
ecutwfc, Ry	70	75	80	80	110
ecutrho, Ry	462	600	640	640	660
k-points	4x4x1	3x3x3	3x3x3	3x3x3	4x4x4

III. RESULTS AND DISCUSSION

A. Energy Comparison

TABLE II: Energies per unit cell

Compound	MoO_3	h-WO_3	o-WO_3	ThO_2
Z	42	74	74	90
$E_{(SR)}$, Ry	-488.98	-885.473	-885.478	-1050.00
$E_{(SOC)}$, Ry	-489.416	-890.391	-890.396	-1062.36
$\Delta E_{(SOC)}$, Ry	-0.4363	-4.9188	-4.9187	-12.3659
$\Delta E_{(SOC)}$, eV	-5.9468	-66.924	-66.922	-168.246

Calculations were performed using both scalar-relativistic (SR) and spin-orbit coupling (SOC) pseudopotentials. The SOC stabilisation energy, defined as $\Delta E_{\mathrm{SOC}} = E_{\mathrm{SOC}} - E_{\mathrm{SR}}$ per cell (Table II), illustrates its strong dependence on atomic number Z, scaling approximately with Z^4. As shown in Table II, ΔE_{SOC} ranges from −6 eV for MoO_3 to roughly −168 eV ThO_2. The two WO_3 phases show similar ΔE_{SOC} values due to their comparable environments. The much larger ΔE_{SOC} value for ThO_2 shows that while SOC is not important for lighter elements, it is essential for an accurate description of heavy elements.

B. Band Structures

Band structures show which electronic energies are allowed in the crystal and are important for determining the band gaps and valence character. When spin-orbit coupling is introduced, degenerate bands split and shift relative to their scalar-relativistic counterparts. The extent of this splitting depends on the atomic species involved – for light atoms like MoO_3 there was no splitting observed. WO_3, which is a heavier atom, does have a slight level of splitting (at around -16.5 eV, 0 eV, 2 eV, as well as at other energy levels).

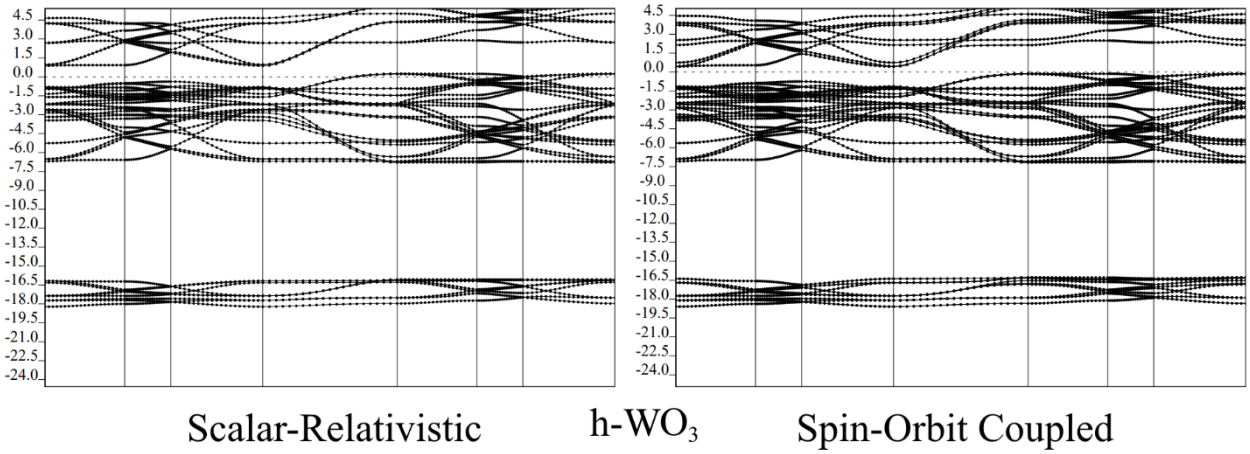

FIG. 1: Band structure of hexagonal WO_3 with two types of pseudopotentials used

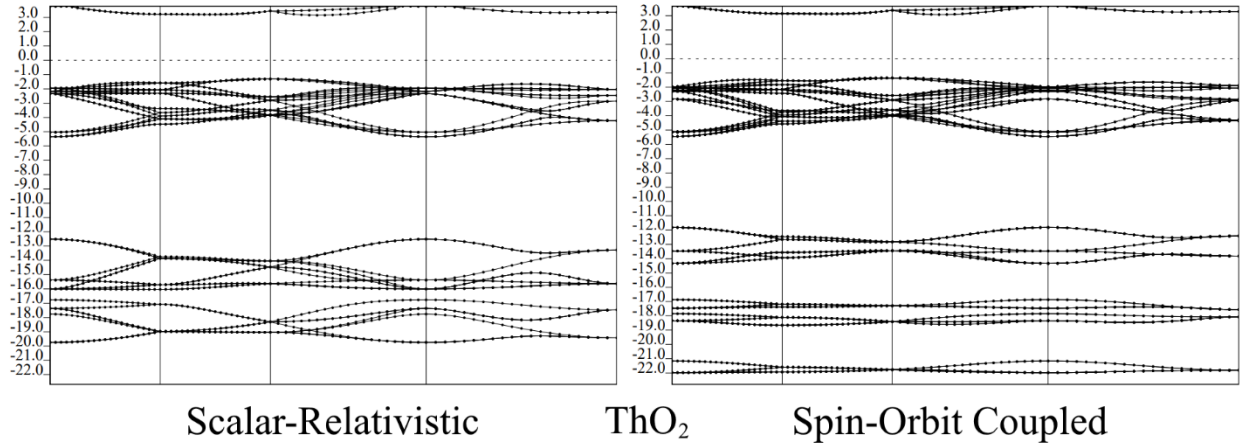

FIG. 2: Band structure of ThO_2 with two types of pseudopotentials used

Bands at lower energies (-20 to -12 eV) split from one large group into three smaller groups. These are dominated by Th 6p and 6s states with some O-2p mixing; SOC splits them, with the upper band belonging to Th $6p_{3/2}$, and the lower

band belonging to Th $6p_{1/2}$. From a materials perspective, this SOC-induced changes affect the energies of excitations and defect levels, so including SOC is essential for any description of its optical spectra and f-electron chemistry.

C. Projected Density of States

The Local Density of States shows the energy distribution and orbital character of electrons – illustrating at which energy values the electrons can exist. Spin-orbit coupling in heavy elements causes peaks found in SR calculations to split into distinct sub-bands based on total angular momentum. The peaks and gaps in the LDOS indicate localised or hybridised states. These control bonding, band gaps, and optical transitions in the material. For heavy elements, the strong relativistic coupling between an electron's spin and its orbital angular momentum lifts the degeneracy of atomic orbitals, causing the single broad peaks seen in scalar-relativistic plots to split into distinct sub-bands corresponding to specific total angular momentum values. In these plots, the lower energy area (up to 0 eV) represents the valence band, while the higher energy region is the conduction band. When it comes to lighter elements (like MoO_3), no visible splitting is seen (as evidenced on the plot).

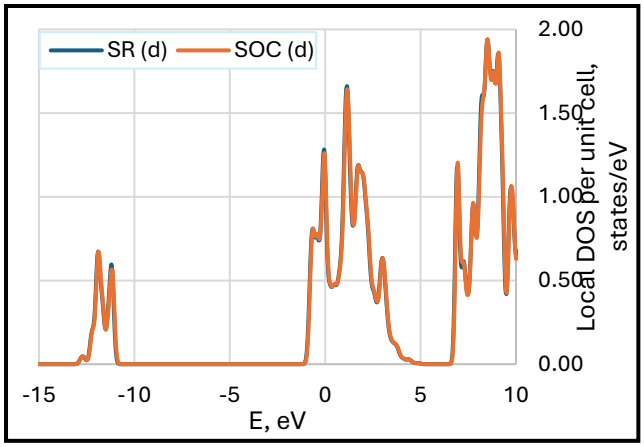

FIG. 3: Density of State plot for d-orbital of MoO_3

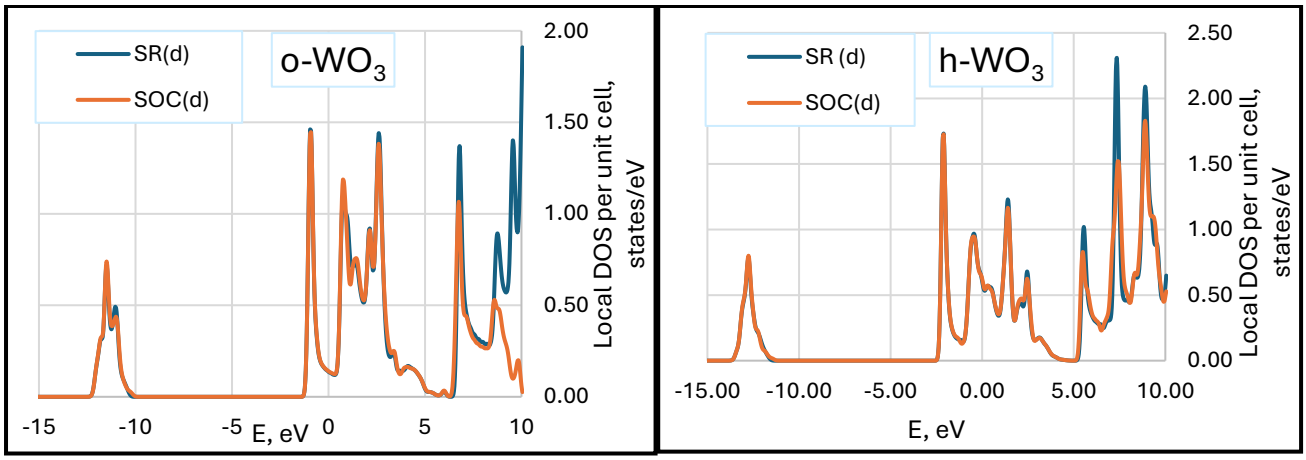

FIG. 4: Density of State plot for d-orbitals of o-WO_3 and h-WO_3

The DOS of WO_3 shows a significant difference in the height of the SR- and SOC-calculated peaks, though their position remains mostly similar. This is different from the results obtained for ThO_2, where both the peak-heights and the peak positions differ from each other, illustrating how using SOC becomes a requirement for heavy atoms if one wishes to get an accurate result.

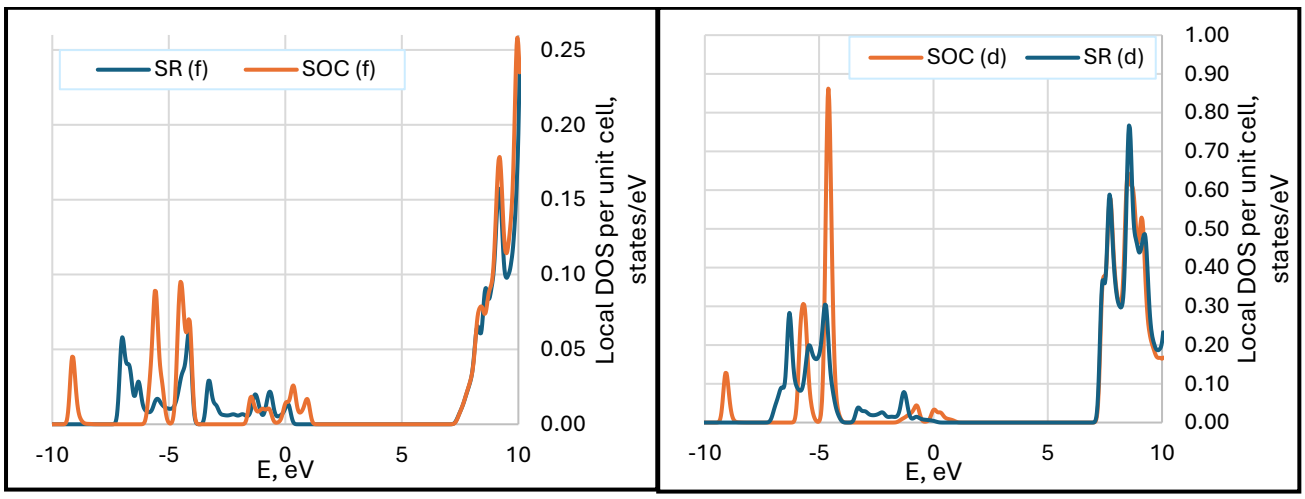

FIG. 5: Density of State plot for f- and d-orbitals of ThO_2

While the conduction band plot (up to 10 eV) shows only a moderate onset of splitting due to the limited energy window, the valence band illustrates the magnitude of relativistic effects. The inclusion of SOC causes the hybridized f- and d-states to shift by approximately 2.5 eV. This shift is significantly larger than the ~0.4 eV splitting observed in WO3, confirming that relativistic effects scale dramatically with atomic number.

The Density of states plots can also be used to illustrate and analyze the differences between the same chemical species of different crystallographic phases. The comparison of the energies lying between the valence and the conducting bands illustrates the differences and the similarities of the two WO_3 phases. The sharper peaks of the hexagonal phase show the more symmetric structure of the crystals, while the broader peaks of the orthorhombic phase arise from the higher level of distortion of the octahedra.

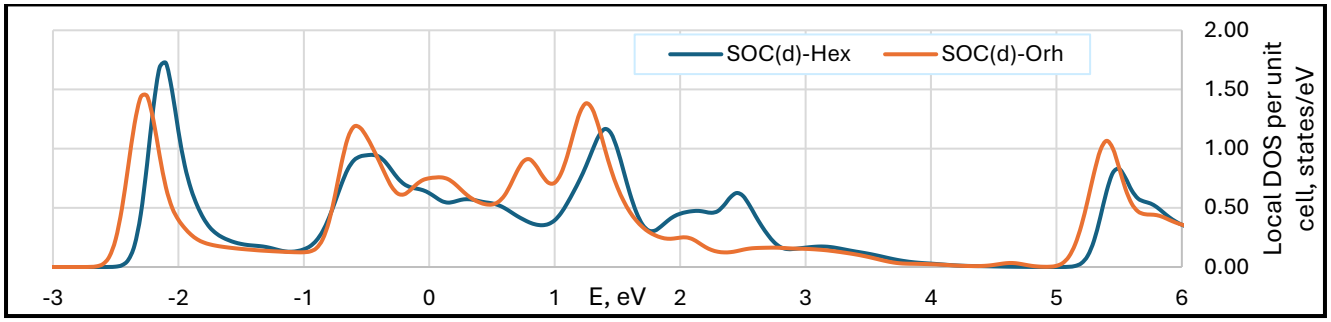

FIG. 6: Aligned density of state plots for the two phases of WO_3

D. Issues with Numerical and Computational Stabilities

During the writing of the project, multiple attempts were made to converge a vc-relax calculation for the monoclinic phase of WO_3 using the SOC PPs. However, this was not achieved, and all the attempts ended in either a divergence or a crash. Another issue was encountered during the calculation of the band structure for WO_3. After about 2.5 hours into the calculation, the virtual machine, along with the host operating system, crashed, causing a "Blue Screen of Death". This issue was solved by running Quantum Espresso natively on Linux.

IV. CONCLUSION

The results of this work confirm the importance of how important relativistic effects become as the atomic number increases. This follows an approximate Z^4 scaling, with the SOC effects being negligible in lighter compounds (like MoO_3) and inducing a minor band-splitting in the heavier WO_3. This contrasts with the heavy actinides like ThO_2, where the SOC effects are so great that any calculation done on these elements must use SOC pseudopotentials, which become absolutely necessary. The illustrated band structure diagramme confirms that, with the lower bands being split to a significant extent.

In addition, the density of states analysis shows similar results – while SOC has a minimal impact on the lighter compounds like MoO_3, it causes a significant shift in the locations of the peaks for the ThO_2.These results demonstrate the importance of spin-orbit coupling specifically, and of relativistic effects in general when dealing with heavy elements.

REFERENCES

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