

# SOC corrected Gaussian basis sets for electronic transport calculations in ANT.Gaussian.

**A. García-Martínez, W. Dednam<sup>1</sup>, S. Pakdel<sup>3</sup>, and J. J. Palacios<sup>2</sup>**

<sup>1</sup> Department of Physics, Science Campus, University of South Africa, Private Bag X6, Florida Park 1710, South Africa

<sup>2</sup> Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, Cantoblanco, Madrid 28049, Spain

<sup>3</sup> Department of Physics, Technical University of Denmark: Kongens Lyngby, Hovedstaden, Denmark

E-mail: dednaw@unisa.ac.za

## Introduction

This is very brief summary of the implementation discussed in Pakdel et al. [1]. There we showed that if a GTO basis set describes properly the band structure of a material in the absence of SOC, then adding SOC as a correction in a post self-consistent-field (SCF) step gives a good approximation to the actual bands when compared to reference methods which produce very high quality results such as VASP [2], Wien2k [3], Quantum Espresso [4] or OpenMX [5–8].

## Details

The Dirac-Kohn-Sham Hamiltonian can be written, to lowest order, simply adding a standard atomic SOC contribution [1] to the SOC-free Kohn-Sham Hamiltonian:

$$\xi(r) \mathbf{L} \cdot \mathbf{S}.$$

When represented in an atomic orbital basis set, it becomes

$$[\xi_{ij} \langle l_i; m_i; s | \mathbf{L} \cdot \mathbf{S} | l_j; m_j; s' \rangle], \quad (1)$$

where

$$\xi_{ij} = \frac{e^2}{2m_e^2 c^2} \int_0^\infty \frac{1}{r} \frac{dV_{\text{eff}}(r)}{dr} R_i(r) R_j^*(r) r^2 dr. \quad (2)$$

In Eq. (2),  $V_{\text{eff}}(r)$  is the effective nuclear potential [1].  $R_i(r)$  are the radial contracted gaussian-type orbitals (CGTOs). Only CGTOs on the same atom and of the same shell type ( $L = 1, 2$  or  $3$ ) contribute to the integral because SOC is an intra-atomic phenomenon [1]. However, for CGTO basis sets with pseudopotentials, a single multiplicative correction to  $\xi_{ij}$  is needed in order to account for the correct effective charge in  $V_{\text{eff}}(r)$  due to the lack of nodal structure near the nucleus in pseudopotentials [1]. Here, we make two minor modifications to improve the above implementation. We use the following Yukawa screening potential:

$$V_{\text{eff}}(r) = \frac{(Z-1) \exp\left(-\frac{\ln Z}{r_c} r\right) + 1}{r} \quad (3)$$

where  $r_c$  is a cutoff, typically the size of an atomic radius ( $\sim 2.5 - 3.0$  a.u.) and  $Z$  is the atomic number. The cutoff varies between shells, being larger for the inner-most shells and smaller for the outer-most ones. For simplicity, we will choose a common value that suits better the shell or shells dominating at the Fermi level (typically  $L = 1, 2$  or  $3$ ), although multiplicative factors can be used to tune the strength of SOC for the other shells. For instance, for transition metals, the strength for  $L = 1$  shells is usually 3-5 times that of the  $L = 2$  shells [9] and this something that may not be caught by a common cutoff radius. .

## FCC Au

Using the `Au_pob_TZVP_rev2` basis set plus additional uncontracted  $s$  primitive and pseudopotential reported in ref. [10], a face-centred cubic (FCC) lattice constant of 4.05 Å and a Monkhorst-Pack (MP)  $k$  mesh of  $32 \times 32 \times 32$  in both our and the reference method, we obtain the SOC-corrected fit of the bands shown in Fig. 1 after setting  $\text{SOCFAC}_P = 150.0$ ,  $\text{SOCFAC}_D = 35.0$  and  $\text{SOCFAC}_F = 5.0$ . For the reference method, we used `Au_PBE19` and `Au7.0-s2p2d2f1` as pseudopotential and basis set, respectively [11].

*SOC factors:*

`SOCFAC_P = 150.0`  
`SOCFAC_D = 35.0`  
`SOCFAC_F = 5.0`

*Basis set:*

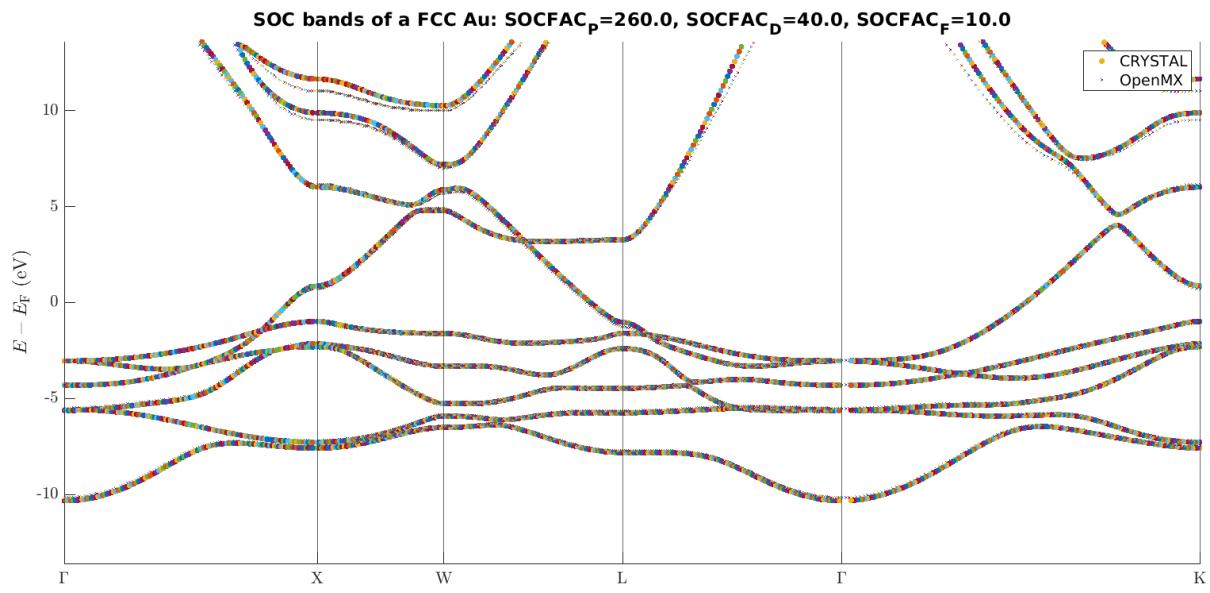
<code>Au 0</code>	
<code>S 3 1.0</code>	
30.0000000000	0.207492311080
27.0000000000	-0.332678933940
14.7468243310	0.383028179580
<code>S 1 1.0</code>	
6.10568239000	1.000000000000
<code>S 1 1.0</code>	
1.13068946000	1.000000000000
<code>S 1 1.0</code>	
0.18001283000	1.000000000000
<code>S 1 1.0</code>	
*0.100000000000	1.000000000000
<code>P 4 1.0</code>	
15.5000000000	0.150017118800
14.0000000000	-0.236098131830
6.42273682050	0.314588969480
1.65956016810	-0.572796704460
<code>P 1 1.0</code>	
0.87155106000	1.000000000000
<code>P 1 1.0</code>	
0.20887895000	1.000000000000
<code>D 4 1.0</code>	
9.55240986560	0.040145559502
7.26988869370	-0.093690906606
1.77464967890	0.317462823170
0.79960541055	0.467951924830
<code>D 1 1.0</code>	
0.55708019000	1.000000000000
<code>D 1 1.0</code>	
0.28104926000	1.000000000000
<code>F 1 1.0</code>	
0.72482000000	1.000000000000

*Built-in Gaussian Pseudopotential:*

Au 0  
mdf60

*Pseudopotential:*

Au 0  
AU-ECP 5 60  
h potential  
1  
2 1.00000000 0.00000000  
s-h potential  
2  
2 13.52321800 426.64186700  
2 6.26438400 36.80066800  
p-h potential  
4  
2 11.41386700 87.00209100  
2 10.32921500 174.00437000  
2 5.70742400 8.87061000  
2 4.82816500 17.90243800  
d-h potential  
4  
2 7.43096300 49.88365500  
2 8.32199000 74.68454900  
2 4.60964200 6.48622700  
2 3.51150700 9.54682100  
f-h potential  
2  
2 3.08463900 8.79164000  
2 3.02474300 11.65845600  
g-h potential  
2  
2 3.97844200 -5.23433700  
2 4.01149100 -6.73814200



**Figure 1.** SOC-corrected bands for face-centred cubic Au obtained using the basis set and pseudopotential reported in ref. [10] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

## Acknowledgments

The computational results contained in this work would also not have been possible without access to the high performance computing (HPC) facility at Unisa, and the supercomputing facility in the Department of Applied Physics at the University of Alicante.

## References

- [1] Pakdel S, Pourfath M and Palacios J J 2018 *Beilstein J. Nanotechnol.* **9** 1015
- [2] Kresse G and Furthmüller J 1996 *Computational Materials Science* **6** 15–50
- [3] Blaha P, Schwarz K, Madsen G, Kvasnicka D and Luitz J 2001 *Wien2k: An augmented plane wave+ local orbitals program for calculating crystal properties* (Karlheinz Schwarz, Techn. Universität Wien, Austria) ISBN 3-9501031-1-2
- [4] Giannozzi P *et al.* 2009 *J. Phys.: Condens. Matter* **21** 395502
- [5] Ozaki T 2003 *Phys. Rev. B* **67**(15) 155108
- [6] Ozaki T and Kino H 2004 *Phys. Rev. B* **69**(19) 195113
- [7] Ozaki T and Kino H 2005 *Phys. Rev. B* **72**(4) 045121
- [8] Ozaki T *et al.* 2017 OpenMX (Open source package for Material eXplorer) ver. 3.8 URL <http://www.openmx-square.org/>
- [9] Barreteau C, Spanjaard D and Desjonquères M C 2016 *Comptes Rendus Physique* **17** 406
- [10] Laun J and Bredow T 2021 *Journal of Computational Chemistry* **42** 1064–1072
- [11] Ozaki T 2019 The database (2019) of fully relativistic pseudopotentials (VPS) and pseudoatomic orbitals (PAO) URL [https://t-ozaki.issp.u-tokyo.ac.jp/vps\\_pao2019/](https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/)