

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

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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 ξ_{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:

`Au 0`

`S 3 1.0`

30.0000000000 0.207492311080

27.0000000000 -0.332678933940

14.7468243310 0.383028179580

`S 1 1.0`

6.10568239000 1.000000000000

`S 1 1.0`

1.13068946000 1.000000000000

`S 1 1.0`

0.18001283000 1.000000000000

`S 1 1.0`

*0.10000000000 1.000000000000

`P 4 1.0`

15.5000000000 0.150017118800

14.0000000000 -0.236098131830

6.42273682050 0.314588969480

1.65956016810 -0.572796704460

`P 1 1.0`

0.87155106000 1.000000000000

`P 1 1.0`

0.20887895000 1.000000000000

`D 4 1.0`

9.55240986560 0.040145559502

7.26988869370 -0.093690906606

1.77464967890 0.317462823170

0.79960541055 0.467951924830

`D 1 1.0`

0.55708019000 1.000000000000

`D 1 1.0`

0.28104926000 1.000000000000

`F 1 1.0`

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

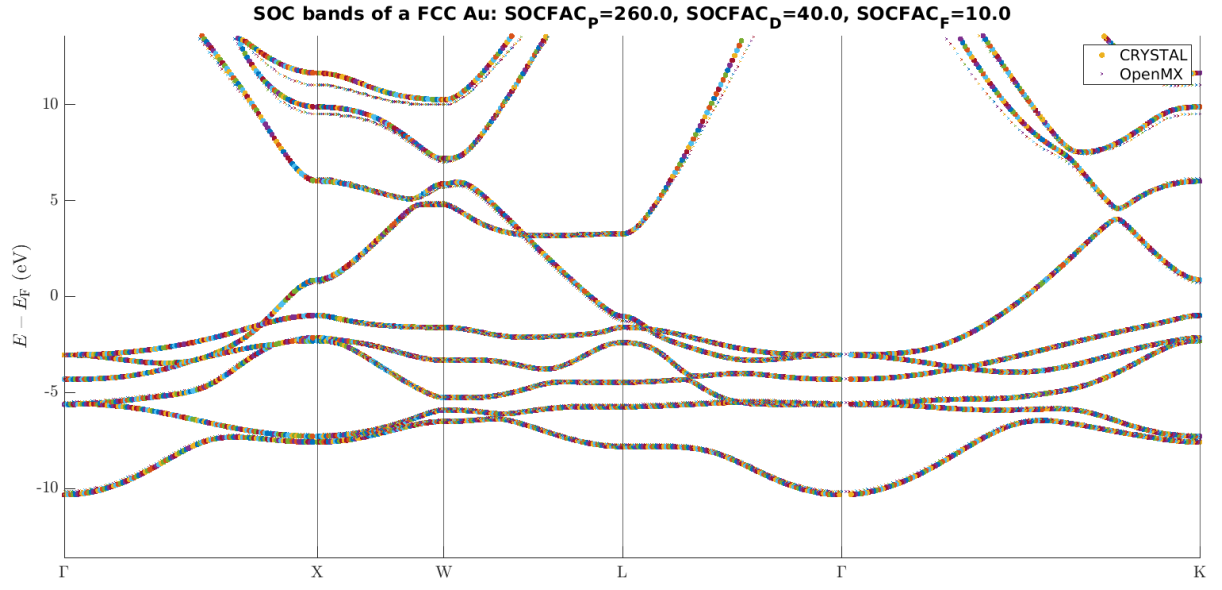


Figure 1. SOC-corrected bands for face-centred cubic Au obtained using the basis set and pseudopotential reported in ref. [10] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

Acknowledgments

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