

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

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Introduction

The Dirac-Kohn-Sham Hamiltonian can be written, to lowest order, as the standard atomic SOC matrix [1] because the radial and angular components of the wave functions in atomic-orbital based DFT, such as the GTOs used by CRYSTAL14 [2] or GAUSSIAN09 [3] are orthogonal:

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

where

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

In Eq. (2), $V_{\text{eff}}(r)$ is the effective nuclear potential [1]. $R_i(r)$ are the radial (un)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 modified Yukawa screening potential:

$$V_{\text{eff}}(r) = \begin{cases} \frac{-(Z-1) \left[\exp\left(-\frac{\ln Z}{r_c} r\right) + 1 \right]}{r} & r \leq r_c \\ \frac{-1}{r} & r > r_c \end{cases} \quad (3)$$

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. Instead of the single global multiplicative factor used in ref. [1], we implement a multiplicative factor for each shell type ($L = 1, 2$ or 3) to account for the fact that the radial SOC coefficients of different shells are usually multiples of each other [4].

Benchmarking

To verify that adding SOC as a correction in a post-SCF step gives good SOC bands, we use Bi(111) bilayers (see Fig. 1 b)) as a test system and compare our calculations using CRYSTAL14

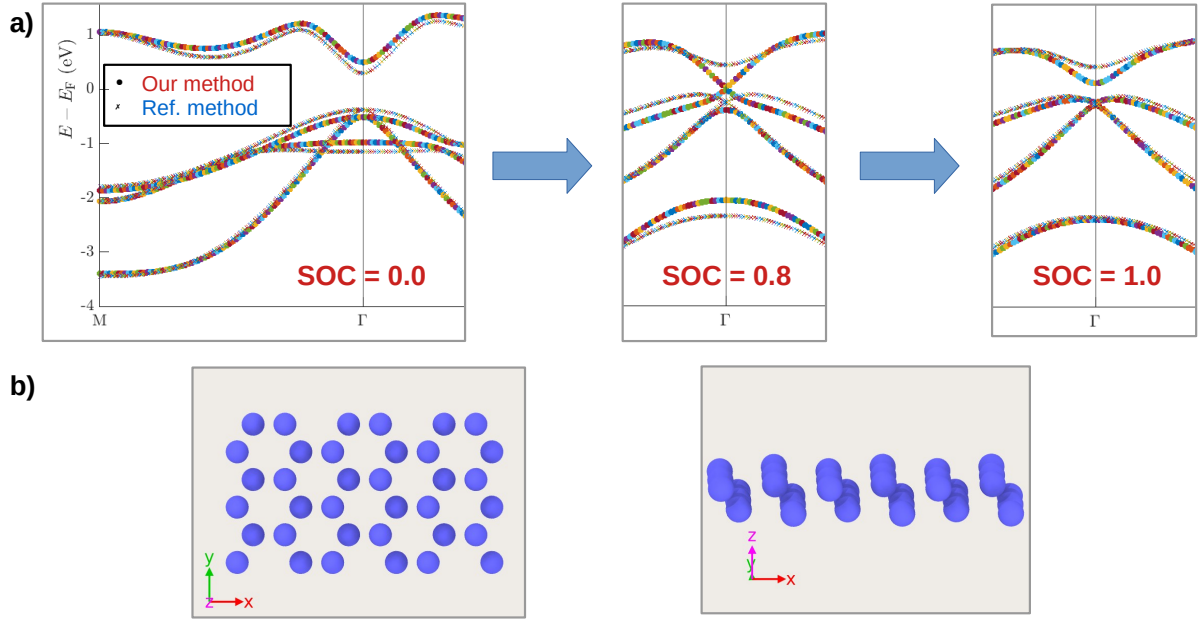


Figure 1. (Colour online) a) Example of adding spin-orbit coupling as a post-SCF correction in DFT calculations of the bands of a solid material, for b) Bismuth (111) bilayers. Solid markers are our method and the fainter crosses correspond to the reference method. The same lattice parameters were used in both methods as in ref. [1]: $a = 4.33 \text{ \AA}$ and $c = 1.74 \text{ \AA}$ in symmetry group $P\bar{3}m1$ of the Hermann-Mauguin classification or space group 164 in the International Tables of Crystallography.

on one hand, and **OpenMX** as reference method, on the other, given the very good agreement between **OpenMX** and **Wien2k** [5, 6].

In Bi(111) bilayers, starting without SOC in the left panel of Fig. 1 a), the band gap must evolve first into a Dirac cone at the Γ point (SOC=0.8 in the middle panel of Fig. 1 a)) and then open up again as SOC is increased to 1.0 in a so-called “band inversion” in the rightmost panel of Fig. 1 a). We used the high quality basis set from ref. [7] for Bi and the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) exchange correlation functional in our **CRYSTAL14** calculation of the bands in the absence of SOC, resulting in reasonable agreement with our reference method, using the **Bi8.0-s4p4d3f2** basis set and **Bi_PBE19** pseudopotential in **OpenMX** [8]. We also used very large k meshes ($81 \times 47 \times 1$), in multiples of 3 to correctly capture the electronic structure at the Γ point. In going from SOC=0.0 to SOC=1.0, we only tuned the multiplicative factor empirically for the bands of p -orbital ($L = 1$ shell) character because only they contribute to SOC ± 4 eV about the Fermi energy. Thus, in Fig. 1, SOC=0.8 corresponds to using a $L = 1$ multiplicative factor $\text{SOCFAC}_P = 270.0$ and SOC=1.0, to $\text{SOCFAC}_P = 350.0$.

The ultimate goal of fitting SOC corrected bands to a reference method is to choose high quality basis sets that can be used in DFT electronic transport calculations where transition metal elements, sometimes with strong SOC, are used as the electrodes. Below follows a database of selected elements for which high quality GTO basis sets have been fitted to our reference method in the presence of SOC using the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) exchange correlation functional consistently throughout. The basis sets can be used as is in our implementation of SOC in **ANT.Gaussian** [9]. **(Note that we have further optimized some of the following basis sets using Billy [10], with the**

asterisks(*) indicating additional and/or optimized Gaussian primitives compared to the original basis set. The asterisks have to be deleted before the basis set can be used in ANT.Gaussian.)

IMPORTANT: Be advised that Gaussian09, unlike CRYSTAL14, removes primitives at random from CGTO shells with more than 7 primitives, and so SOC results may not be accurate for basis sets containing $L = 1, 2$ or 3 CGTO shells with more than 7 primitives.

FCC Aluminum

Using the `Al_pob_DZVP_rev2` all-electron basis set reported in ref. [11], 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. 2 after setting both SOCFAC_P and SOCFAC_D to a value of 1.0. For the reference method, we used `Al_PBE19` and `Al7.0-s3p3d2` as pseudopotential and basis set, respectively [8].

SOC factors:

`SOCFAC_P` = 1.0

`SOCFAC_D` = 1.0

All-electron basis set:

`Al 0`

`S 5 1.0`

5887.5727030	0.0013483347987
885.61225996	0.0100715768090
201.13604899	0.0451324540560
56.284974674	0.1146126804300
17.229551243	0.1015960894300

`S 3 1.0`

29.340249922	0.0693474542080
3.0439630420	-0.4252811767900
1.1285539518	-0.4144983221000

`S 1 1.0`

0.7834298000	1.00000000000000
--------------	------------------

`S 1 1.0`

0.1440019200	1.00000000000000
--------------	------------------

`P 5 1.0`

145.11918809	0.0063963373134
33.717894833	0.0441893599650
10.369863083	0.1558157599300
3.5135616036	0.2863528695100
1.1980050273	0.2292142324800

`P 1 1.0`

0.3200672400	1.00000000000000
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`P 1 1.0`

0.1500336200	1.00000000000000
--------------	------------------

`D 1 1.0`

0.1530089300	1.00000000000000
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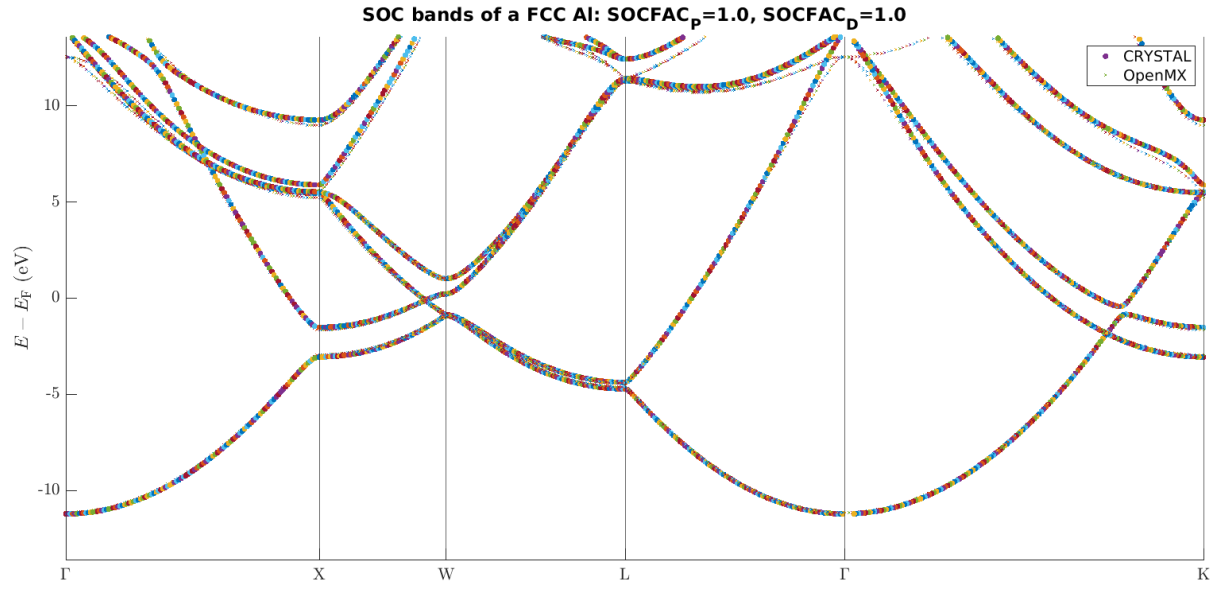


Figure 2. SOC-corrected bands for face-centred cubic Al obtained using the all-electron basis set reported in ref. [11] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

FCC Copper

Using the `Cu.extended.ruiz.2003` all-electron basis set [12], a FCC lattice constant of 3.63 Å, and a 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. 3 with $\text{SOCFAC}_P = \text{SOCFAC}_D = 1.0$. For the reference method, we used `Cu.PBE19H` and `Cu6.0H-s3p3d3f1` as pseudopotential and basis set, respectively [8].

SOC factors:

`SOCFAC_P = 1.0`

`SOCFAC_D = 1.0`

All-electron basis set:

`Cu 0`

`S 6 1.0`

76441.483694 0.0014236548869

11477.790484 0.010910644019

2611.4773990 0.054139319495

737.33531101 0.18863206957

240.02819227 0.38341646126

82.721112667 0.29645681555

`S 3 1.0`

160.07447183 -0.11037499013

18.854087693 0.64586203973

7.7438526664 0.44511050812

`S 2 1.0`

13.678658833 -0.22684755916

2.2583597115 0.72397240174

`S 1 1.0`

.92525661579 1.0000000000

`S 1 1.0`

.41000000000 1.0000000000

`S 1 1.0`

.18000000000 1.0000000000

`P 3 1.0`

2530.0174404 0.0019142187743

600.09192696 0.015800163021

194.09448024 0.076268471159

`P 3 1.0`

73.686313161 0.23880092118

30.458500032 0.44974987602

13.130879763 0.39361952224

`P 1 1.0`

5.5263086949 1.0000000000

`P 1 1.0`

2.1487388219 1.0000000000

`P 1 1.0`

*0.8145 1.0000000000

`P 1 1.0`

*0.1327 1.0000000000

`D 3 1.0`

```

51.443304983 0.029319456167
14.404225180 0.15699236141
4.8477556014 0.37790966643
D 1 1.0
1.6194940205 1.0000000000
D 1 1.0
*0.4664 1.0000000000

```

Note that the asterisks (*) have to be deleted before the basis set can be used in ANT.Gaussian.

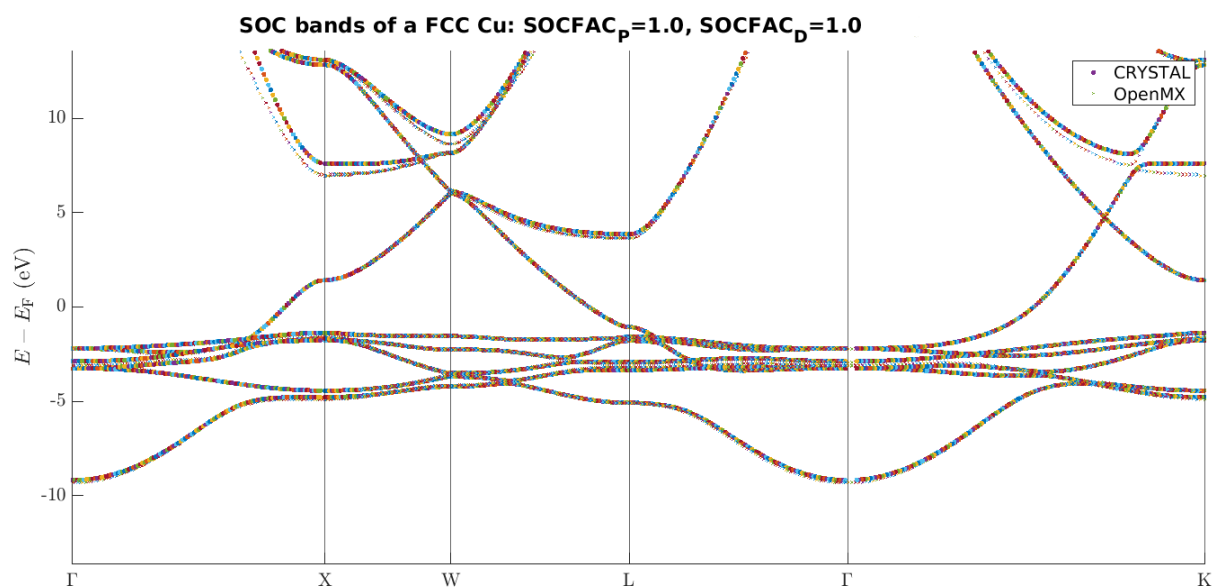


Figure 3. SOC-corrected bands for face-centred cubic Cu obtained using the all-electron basis set reported in ref. [12] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

FCC Silver

Using the Ag_pob.DZVP_2018 basis set and pseudopotential reported in ref. [13], a face-centred cubic (FCC) lattice constant of 4.075 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. 4 after setting $\text{SOCFAC}_P = 80.0$, $\text{SOCFAC}_D = 10.0$ and $\text{SOCFAC}_F = 5.0$. For the reference method, we used Ag_PBE19 and Ag7.0-s3p3d2f2 as pseudopotential and basis set, respectively [8].

SOC factors:

$\text{SOCFAC}_P = 80.0$

$\text{SOCFAC}_D = 10.0$

$\text{SOCFAC}_F = 5.0$

Basis set:

Ag 0

S 3 1.0

9.08844200000 -1.980891879700

7.54073100000 2.755451334700

2.79400500000 0.227154083810

S 1 1.0

1.23043317000 1.000000000000

S 1 1.0

0.18387114000 1.000000000000

P 4 1.0

4.45124000000 -0.993521037710

3.67526300000 1.050052523700

1.26106209050 0.647475325370

0.54212477498 0.256215507230

P 1 1.0

0.15011983000 1.000000000000

D 4 1.0

7.79566722920 -0.017042912377

2.89265102380 0.234461548030

1.24742732030 0.447658775330

0.49313817671 0.390649545600

D 1 1.0

0.15938987000 1.000000000000

F 1 1.0

1.39711000000 1.000000000000

Pseudopotential:

Ag 0

AG-ECP 4 28

g potential

1

2 1.0000000 0.0000000

s-g potential

2

2 12.5677140 255.0547710

2 6.9976620 36.9833930

p-g potential

4

2 11.3164960 60.7157050

2 10.9580630 121.4438890

2 7.1114000 10.1718660

2 6.7733190 20.4865640

d-g potential

4

2 8.9284370 29.5049380

2 11.1025670 44.0187360

2 5.5432120 5.3683330

2 3.9288350 7.4083750

f-g potential

2

2 11.0129130 -12.6234030

2 11.0198980 -16.7643270

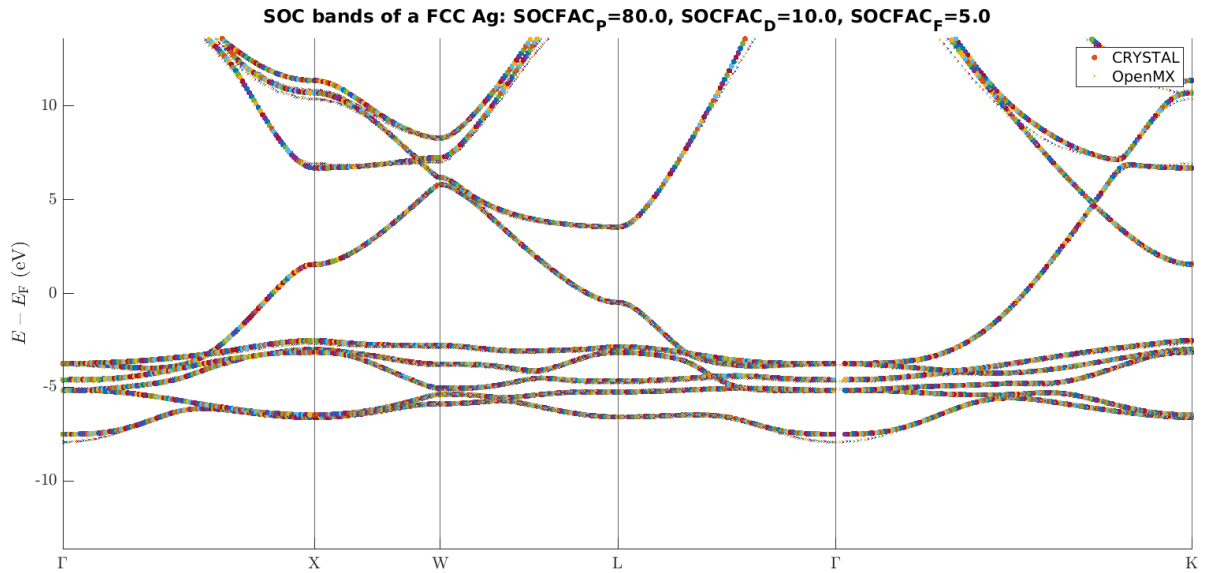


Figure 4. SOC-corrected bands for face-centred cubic Ag obtained using the basis set and pseudopotential reported in ref. [13] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

Antimonene: a Sb(111) bilayer

Using the `Sb_pob_TZVP_2018` basis set and pseudopotential reported in ref. [13], a Sb(111) bilayer similar to Fig. 1, with lattice parameters of $a = 4.12 \text{ \AA}$ and $c = 1.64 \text{ \AA}$ and a Monkhorst-Pack (MP) k mesh of $81 \times 47 \times 1$ in both our and the reference method, we obtain the SOC-corrected fit of the bands shown in Fig. 5 after setting both $\text{SOCFAC}_P = 90.0$ and $\text{SOCFAC}_D = 5.0$. For the reference method, we used `Sb_PBE19` and `Sb7.0-s3p3d3f2` as pseudopotential and basis set, respectively [8].

SOC factors:

`SOCFAC_P` = 90.0

`SOCFAC_D` = 5.0

Basis set:

Sb 0

S 4 1.0

1612.41999330	0.000285403808
238.844520970	0.001339377875
23.9981188090	-0.049388154574
15.1931242130	0.433922272540

S 2 1.0

11.7364097330	0.921255199650
6.52597747940	0.792352802260

S 1 1.0

1.58348739000	1.000000000000
---------------	----------------

S 1 1.0

0.18345132000	1.000000000000
---------------	----------------

P 3 1.0

215.683933540	0.000260518232
16.3744790880	0.073728000195
9.72162833450	-0.272300281280

P 3 1.0

2.79826431540	0.464726923740
1.47110450330	0.503642420750
0.75165385301	0.187066662940

P 1 1.0

0.37211239000	1.000000000000
---------------	----------------

P 1 1.0

0.12000001000	1.000000000000
---------------	----------------

D 6 1.0

115.903122530	0.000531409151
30.4742337200	0.005941113917
18.2284182390	-0.010563706947
4.32914566460	0.203481773410
2.12948184960	0.427483789280
0.99682636692	0.385395608090

D 1 1.0

0.62366245000	1.000000000000
---------------	----------------

D 1 1.0

0.31224235000	1.000000000000
---------------	----------------

D 1 1.0

0.12000012000

1.000000000000

Pseudopotential:

```

Sb      0
SB-ECP   4      28
g potential
  1
2      1.0000000      0.0000000
s-g potential
  2
2      16.3308650      281.0715810
2      8.5565420      61.7166040
p-g potential
  4
2      14.4703370      67.4573800
2      13.8161940      134.9335030
2      8.4249240      14.7163440
2      8.0927280      29.5185120
d-g potential
  4
2      14.8863310      35.4478150
2      15.1463190      53.1434660
2      5.9082670      9.1792230
2      5.5943220      13.2402530
f-g potential
  2
2      14.4449780      -15.3668010
2      14.4492950      -20.2961380

```

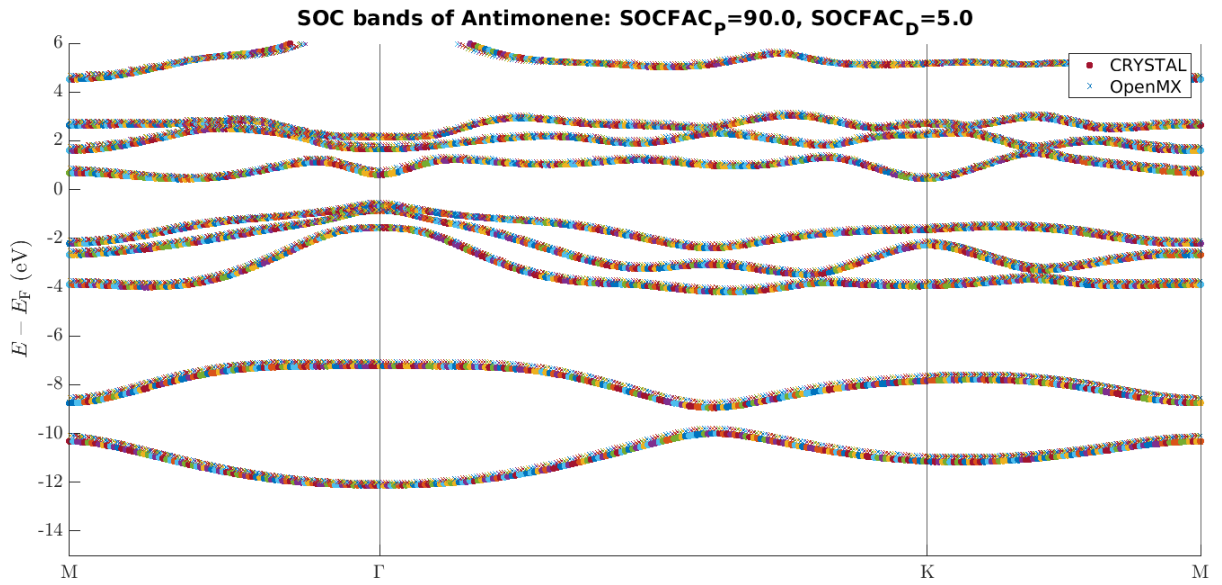


Figure 5. SOC-corrected bands for Sb(111) obtained using the basis set and pseudopotential reported in ref. [13] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

BCC Tungsten

Using the `W_pob.TZVP_rev2.s` basis set and pseudopotential reported in ref. [7], a body-centred cubic (BCC) lattice constant of 3.16 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. 6 after setting $\text{SOCFAC}_P = 240.0$, $\text{SOCFAC}_D = 30.0$ and $\text{SOCFAC}_F = 10.0$. For the reference method, we used `W_PBE19` and `W7.0-s3p2d2f1` as pseudopotential and basis set, respectively [8].

SOC factors:

`SOCFAC_P = 240.0`

`SOCFAC_D = 30.0`

`SOCFAC_F = 10.0`

Basis set:

`W 0`

`S 3 1.0`

30.0000000000 0.322464834100

27.0000000000 -0.466922572140

13.0780456840 0.426995637760

`S 1 1.0`

4.56489858000 1.000000000000

`S 1 1.0`

*0.92909758000 1.000000000000

`S 1 1.0`

*0.2029 1.000000000000

`S 1 1.0`

*0.117 1.000000000000

`P 4 1.0`

17.3684 -0.0364

12.4136 0.1092

5.15862176580 -0.293999550200

1.2804 0.5082

`P 1 1.0`

*0.6577 1.000000000000

`P 1 1.0`

*0.245 1.000000000000

`D 4 1.0`

7.40647373150 0.086993963018

5.90262686030 -0.176675400110

1.29847567500 0.551456970300

0.57153508541 0.953135965350

`D 1 1.0`

*0.4269 1.000000000000

`D 1 1.0`

*0.2466 1.000000000000

`F 1 1.0`

*0.3026 1.000000000000

Pseudopotential:

W 0

ECP60MDF 5 60

H-Komponente

1

2 1.000000 0.000000

S-H

2

2 11.063795 419.227599

2 8.217641 41.191307

P-H

6

2 9.338188 107.348110

2 8.430448 214.699568

4 9.490020 0.025442

4 9.489947 0.051895

2 1.882997 -0.117184

2 1.906972 0.296689

D-H

6

2 6.205433 58.881279

2 6.122157 98.683556

4 6.274556 0.019537

4 6.226375 0.021956

2 1.963875 -0.088577

2 1.888287 -0.209726

F-H

2

2 2.307953 6.232472

2 2.270609 8.311345

G-H

2

2 3.583491 -6.802944

2 3.562515 -8.443232

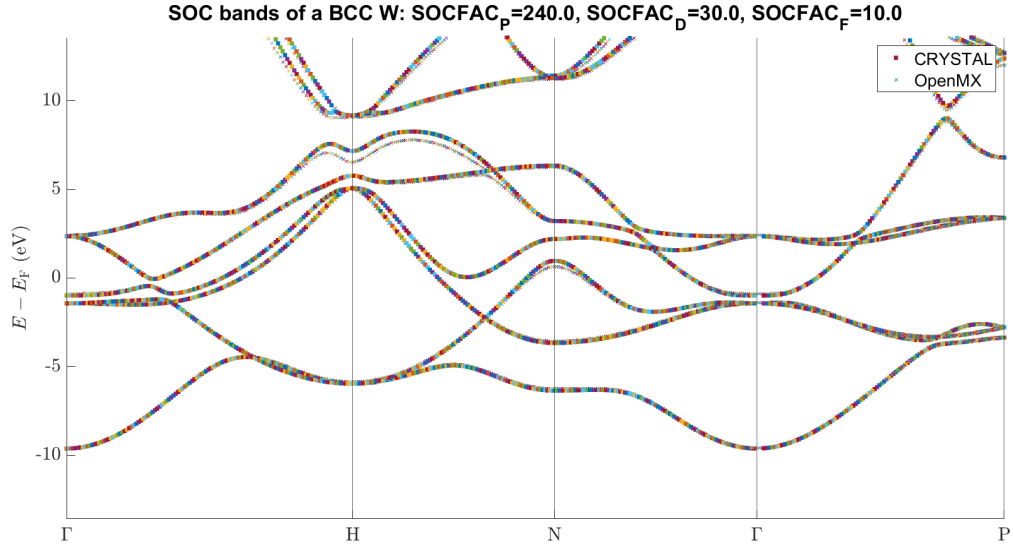


Figure 6. SOC-corrected bands for body-centred cubic W obtained using the basis set and pseudopotential reported in ref. [7] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

FCC Platinum

Using the Pt_pob_TZVP_rev2 basis set and pseudopotential reported in ref. [7], a face-centred cubic (FCC) lattice constant of 3.91 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. 7 after setting $\text{SOCFAC}_P = 280.0$, $\text{SOCFAC}_D = 40.0$ and $\text{SOCFAC}_F = 10.0$. For the reference method, we used Pt_PBE19 and Pt7.0-s2p2d2f1 as pseudopotential and basis set, respectively [8].

SOC factors:

$\text{SOCFAC}_P = 280.0$

$\text{SOCFAC}_D = 40.0$

$\text{SOCFAC}_F = 10.0$

Basis set:

Pt 0

S 3 1.0

30.0000000000	0.271482639000
27.0000000000	-0.422267587740
14.4083185640	0.443615819950

S 1 1.0

5.76260815000	1.000000000000
---------------	----------------

S 1 1.0

1.06835871000	1.000000000000
---------------	----------------

S 1 1.0

0.15368971000	1.000000000000
---------------	----------------

P 4 1.0

15.5000000000	-0.156727186290
14.0000000000	0.238534129890
6.11612123390	-0.310413797330
1.57155863850	0.564735250890

P 1 1.0

0.77232013000	1.000000000000
---------------	----------------

P 1 1.0

0.25285881000	1.000000000000
---------------	----------------

D 4 1.0

8.32079376110	0.062945798646
7.42072265200	-0.090271847072
1.65704106390	0.168125264160
0.73943569960	0.250454169700

D 1 1.0

1.12524984000	1.000000000000
---------------	----------------

D 1 1.0

0.27562365000	1.000000000000
---------------	----------------

F 1 1.0

0.56813000000	1.000000000000
---------------	----------------

Pseudopotential:

Pt 0

PT-ECP 5 60

h potential

1

2	1.00000000	0.00000000
---	------------	------------

s-h potential

2

2	14.60450000	429.64608700
---	-------------	--------------

2	7.21828700	73.15688400
---	------------	-------------

p-h potential

4

2	11.57716200	88.02291700
---	-------------	-------------

2	10.88384300	175.99819600
---	-------------	--------------

2	6.42440300	13.68227400
---	------------	-------------

2	5.22419800	27.41465100
---	------------	-------------

d-h potential

4

2	7.69961000	43.55785200
---	------------	-------------

2	7.55080800	65.36910800
---	------------	-------------

2	3.96116400	7.01859600
---	------------	------------

2	3.87277700	11.39173300
---	------------	-------------

f-h potential

2

2	3.37986900	10.71022000
---	------------	-------------

2	3.32625500	14.27812500
---	------------	-------------

g-h potential

2

2	5.45202000	-11.65174900
---	------------	--------------

2	5.41258500	-14.37552500
---	------------	--------------

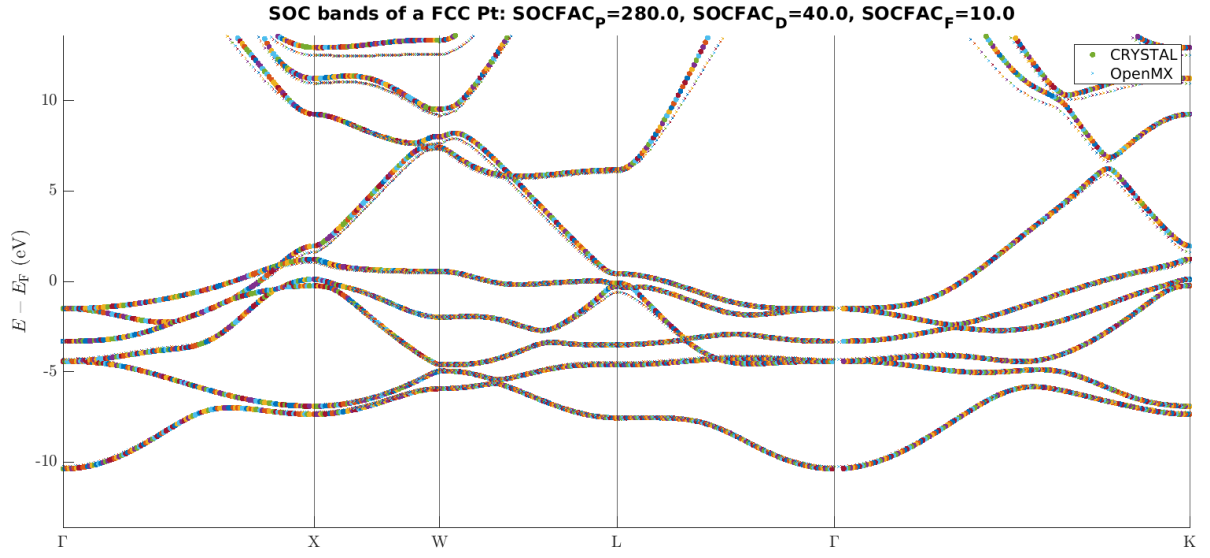


Figure 7. SOC-corrected bands for face-centred cubic Pt obtained using the basis set and pseudopotential reported in ref. [7] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

FCC Au

Using the `Au_pob_TZVP_rev2` basis set plus additional uncontracted s primitive and pseudopotential reported in ref. [7], 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. 8 after setting $\text{SOCFAC}_P = 260.0$, $\text{SOCFAC}_D = 40.0$ and $\text{SOCFAC}_F = 10.0$. For the reference method, we used `Au_PBE19` and `Au7.0-s2p2d2f1` as pseudopotential and basis set, respectively [8].

SOC factors:

`SOCFAC_P` = 260.0

`SOCFAC_D` = 40.0

`SOCFAC_F` = 10.0

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

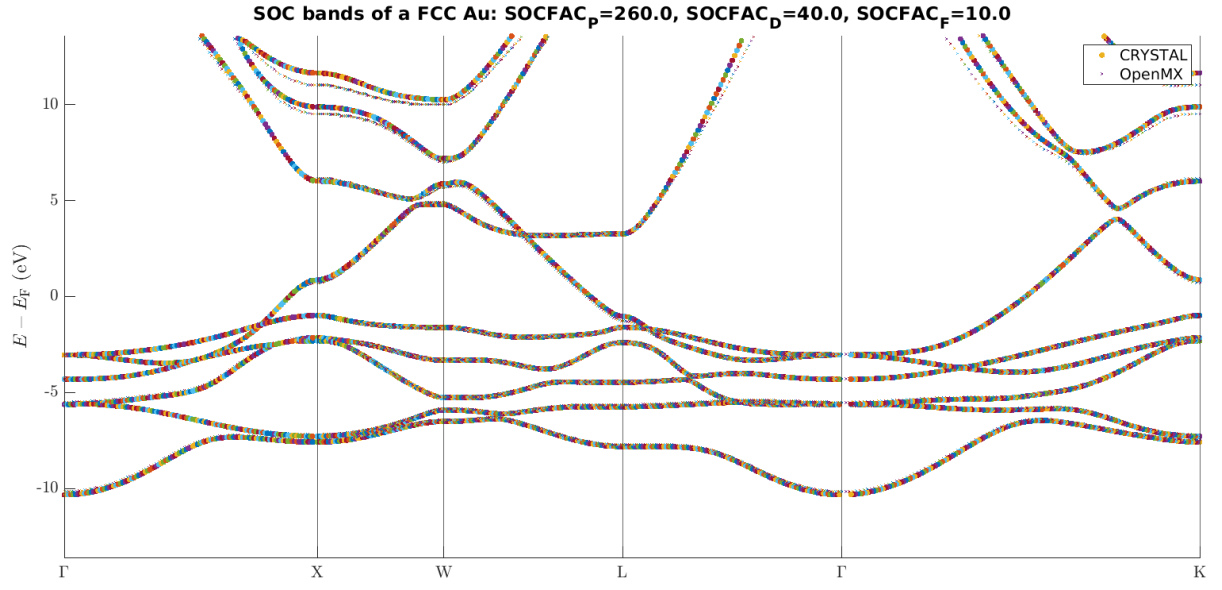


Figure 8. SOC-corrected bands for face-centred cubic Au obtained using the basis set and pseudopotential reported in ref. [7] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

FCC Pb

Using the Pb.ECP60MDF_baranek.2013 basis set with optimized uncontracted s , p , d and f primitives and the pseudopotential reported in ref. [14], a face-centred cubic (FCC) lattice constant of 4.93 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. 8 after setting $\text{SOCFAC}_P = 260.0$, $\text{SOCFAC}_D = 50.0$ and $\text{SOCFAC}_F = 0.0$. For the reference method, we used Pb_PBE19 and Pb8.0-s3p3d3f2 as pseudopotential and basis set, respectively [8].

SOC factors:

$\text{SOCFAC}_P = 260.0$

$\text{SOCFAC}_D = 50.0$

$\text{SOCFAC}_F = 0.0$

Basis set:

Pb 0

S 6 1.00

8.55351735988 3.88475299531

7.35277444701 -5.11944720447

2.95283552202 0.359342355194

1.43101525276 2.0148141461

0.659101026799 0.477751455641

0.220157140772 -0.029791382408

S 1 1.00

*1.2543 1.0

S 1 1.00

*0.4504 1.0

S 1 1.00

*0.147 1.0

P 6 1.00

8.55351735988 3.13503035185

7.35277444701 -4.65435922478

2.95283552202 1.34852524939

1.43101525276 3.23612718594

0.659101026799 1.35196984634

0.220157140772 0.0649906557872

P 1 1.00

*1.2879 1.0

P 1 1.00

*0.5176 1.0

P 1 1.00

*0.1325 1.0

D 5 1.00

11.1394028684 0.299749731795

7.57317950313 -0.908307739883

2.21243848295 3.44990840575

1.0927431021 5.08865830004

0.517878712738 3.46485836421

D 1 1.00

*0.2314 1.0

F 1 1.00

*0.1354 1.0

Built-in Gaussian Pseudopotential:

Pb 0
mdf60

Pseudopotential:

Pb 0
PB-ECP 4 60
g potential
1
2 1.00000000 0.00000000
s-g potential
2
2 12.29630300 281.28549900
2 8.63263400 62.52021700
p-g potential
4
2 10.24179000 72.27689700
2 8.92417600 144.59108300
2 6.58134200 4.75869300
2 6.25540300 9.94062100
d-g potential
4
2 7.75433600 35.84850700
2 7.72028100 53.72434200
2 4.97026400 10.11525600
2 4.56378900 14.83373100
f-g potential
2
2 3.88751200 12.20989200
2 3.81196300 16.19029100

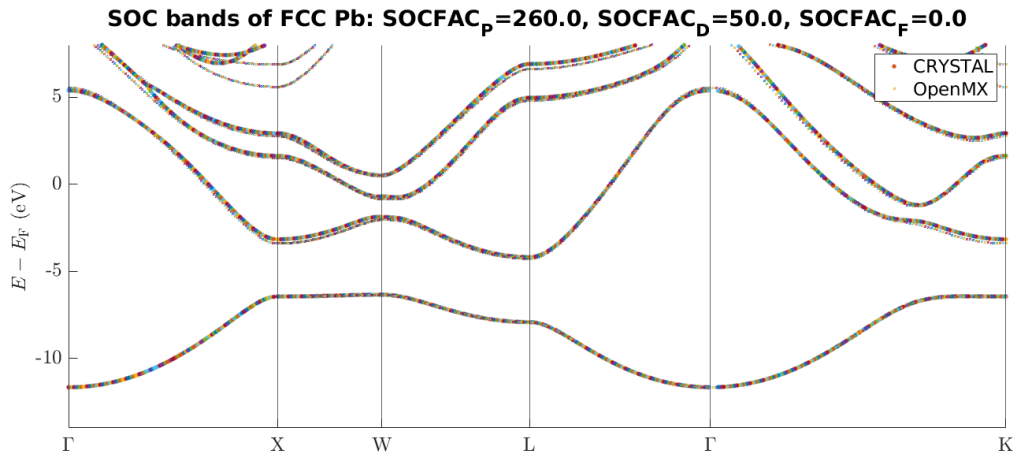


Figure 9. SOC-corrected bands for face-centred cubic Pb obtained using the basis set and pseudopotential reported in ref. [14] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

Bi(111) bilayer

Using the Bi_pob_TZVP_rev2 basis set plus additional uncontracted s primitive and pseudopotential reported in ref. [7], the Bi(111) bilayer shown in Fig. 1, with lattice parameters of $a = 4.33 \text{ \AA}$ and $c = 1.74 \text{ \AA}$ and a Monkhorst-Pack (MP) k mesh of $81 \times 47 \times 1$ in both our and the reference method, we obtain the SOC-corrected fit of the bands shown in Fig. 10 after setting both $\text{SOCFAC}_P = 340.0$ and $\text{SOCFAC}_D = 120.0$. For the reference method, we used Bi_PBE19 and Bi8.0-s3p3d3f2 as pseudopotential and basis set, respectively [8].

SOC factors:

$\text{SOCFAC}_P = 340.0$

$\text{SOCFAC}_D = 120.0$

Basis set:

Bi 0

S 4 1.0

716.414353100	0.000312543071
83.8060590470	0.001762476895
21.1169628530	-0.219109834370
15.4914481870	0.404112249310

S 2 1.0

23.2398550290	-0.068255758685
6.64742550000	0.978880464710

S 2 1.0

1.96177440000	0.653863290000
0.97252866000	0.346136700000

S 1 1.0

0.20618896000	1.000000000000
---------------	----------------

S 1 1.0

*0.100000000000	1.000000000000
-----------------	----------------

P 3 1.0

15.2496446690	0.745603560000
14.8461760530	-0.855786373380
7.06368267840	0.401491595920

P 3 1.0

2.58812556160	0.355427296330
1.50202084990	0.639769918900
0.76732724388	0.323327738390

P 1 1.0

0.42288904000	1.000000000000
---------------	----------------

P 1 1.0

0.17062087000	1.000000000000
---------------	----------------

D 6 1.0

66.4044819480	0.000381028783
13.8584269610	0.010746152442
7.06545190000	-0.071947646845
2.52521440350	0.261959749890
1.34195850000	0.425947500000
0.68340941000	0.336803256270

D 1 1.0

0.90438000000	1.000000000000
---------------	----------------

D 1 1.0		
0.41457000000	1.000000000000	
D 1 1.0		
0.15146817000	1.000000000000	

Pseudopotential:

Bi	0	
BI-ECP	5	60
h potential		
1		
2	1.0000000	0.0000000
s-h potential		
2		
2	13.0430900	283.2642270
2	8.2216820	62.4719590
p-h potential		
4		
2	10.4677770	72.0014990
2	9.1189010	144.0022770
2	6.7547910	5.0079450
2	6.2525920	9.9915500
d-h potential		
4		
2	8.0814740	36.3962590
2	7.8905950	54.5976640
2	4.9555560	9.9842940
2	4.7045590	14.9814850
f-h potential		
2		
2	4.2145460	13.7133830
2	4.1334000	18.1943080
g-h potential		
2		
2	6.2057090	-10.2474430
2	6.2277820	-12.9557100

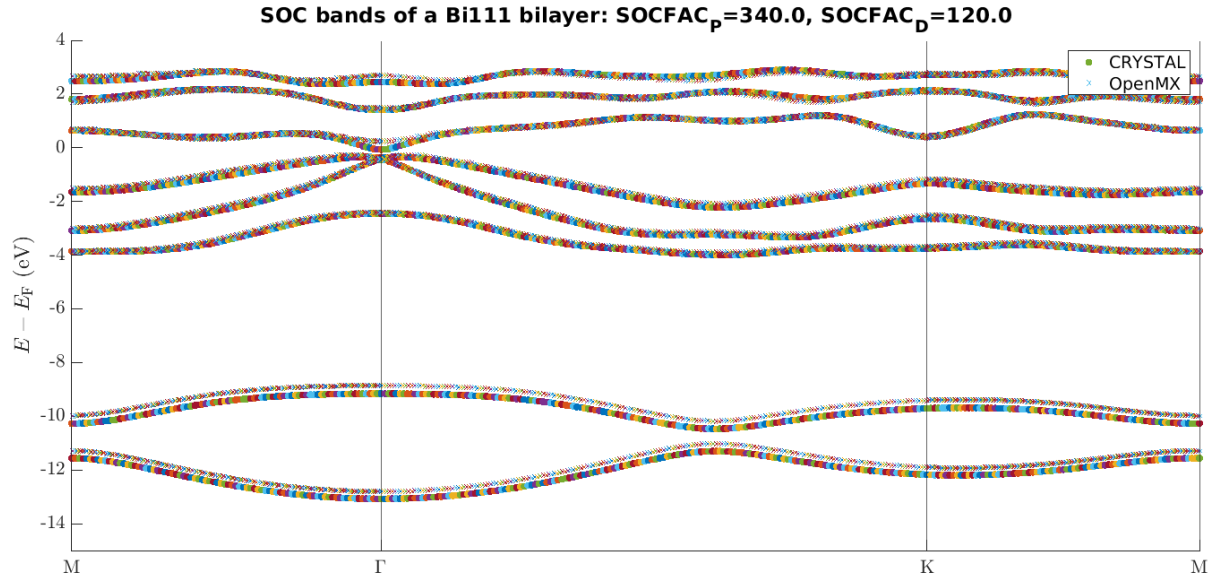


Figure 10. SOC-corrected bands for Bi(111) obtained using the basis set and pseudopotential reported in ref. [7] in CRYSTAL14 (solid markers) and the reference method OpenMX (faint crosses).

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] Dovesi R *et al.* 2014 *Int. J. Quantum Chem.* **114** 1287
- [3] Frisch M J *et al.* Computer code GAUSSIAN09, Revision C.01, Gaussian, Inc. Wallingford, CT, 2009
- [4] Barreteau C, Spanjaard D and Desjonquères M C 2016 *Comptes Rendus Physique* **17** 406
- [5] Lejaeghere K *et al.* 2016 *Science* **351** aad3000
- [6] Ozaki T 2019 Delta gauge of OpenMX with the database (2019) URL https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/Delta_Factor/index.html
- [7] Laun J and Bredow T 2021 *Journal of Computational Chemistry* **42** 1064–1072
- [8] Ozaki T 2019 The database (2019) of fully relativistic pseudopotentials (VPS) and pseudo-atomic orbitals (PAO) URL https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/
- [9] Palacios J J *et al.* 2018 Computer code ANT.Gaussian, with SOC corrections Available from <https://github.com/juanjosepalacios/ANT.Gaussian>
- [10] Towler M 2017 Computer program billy used for optimizing valence basis functions and/or performing simple geometric optimizations with CRYSTAL95/98/03/06/09/14. Available from <https://vallico.net/mike-towler/crystal.html>
- [11] Vilela Oliveira D, Laun J, Peintinger M F and Bredow T 2019 *Journal of Computational Chemistry* **40** 2364–2376
- [12] Ruiz E, Llunell M and Alemany P 2003 *Journal of Solid State Chemistry* **176** 400–411
- [13] Laun J, Vilela Oliveira D and Bredow T 2018 *Journal of Computational Chemistry* **39** 1285–1290
- [14] Sophia G, Baranek P, Sarrazin C, Rérat M and Dovesi R 2013 *Phase Transitions* **86** 1069–1084