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:

$$\xi\left(r\right)\mathbf{L}\cdot\mathbf{S}=\left[\xi_{\mathrm{ij}}\left\langle l_{\mathrm{i}};m_{l_{\mathrm{i}}};s|\mathbf{L}\cdot\mathbf{S}|l_{\mathrm{j}};m_{l_{\mathrm{j}}};s'\right\rangle\right], \tag{1}$$

where

$$\xi_{\mathrm{ij}}=\frac{e^2}{2m_e^2c^2}\int_0^\infty\frac{1}{r}\frac{\mathrm{d}V_{\mathrm{eff}}\left(r\right)}{\mathrm{d}r}R_{\mathrm{i}}\left(r\right)R_{\mathrm{j}}^*\left(r\right)r^2\mathrm{d}r. \tag{2}$$

In Eq. (2), $V_{\mathrm{eff}}\left(r\right)$ is the effective nuclear potential [1]. $R_{\mathrm{i}}\left(r\right)$ 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 $V_{\mathrm{eff}}\left(r\right)$ 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:

$$V_{\mathrm{eff}}\left(r\right)=\frac{\left(Z-1\right)\exp\left(-\frac{lnZ}{r_c}r\right)+1}{r} \tag{3}$$

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 [4] 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. [5], 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 $\mathrm{SOCFAC}_P = 150.0$, $\mathrm{SOCFAC}_D = 35.0$ and $\mathrm{SOCFAC}_F = 5.0$. For the reference method, we used `Au_PBE19` and `Au7.0-s2p2d2f1` as pseudopotential and basis set, respectively [6].

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
```

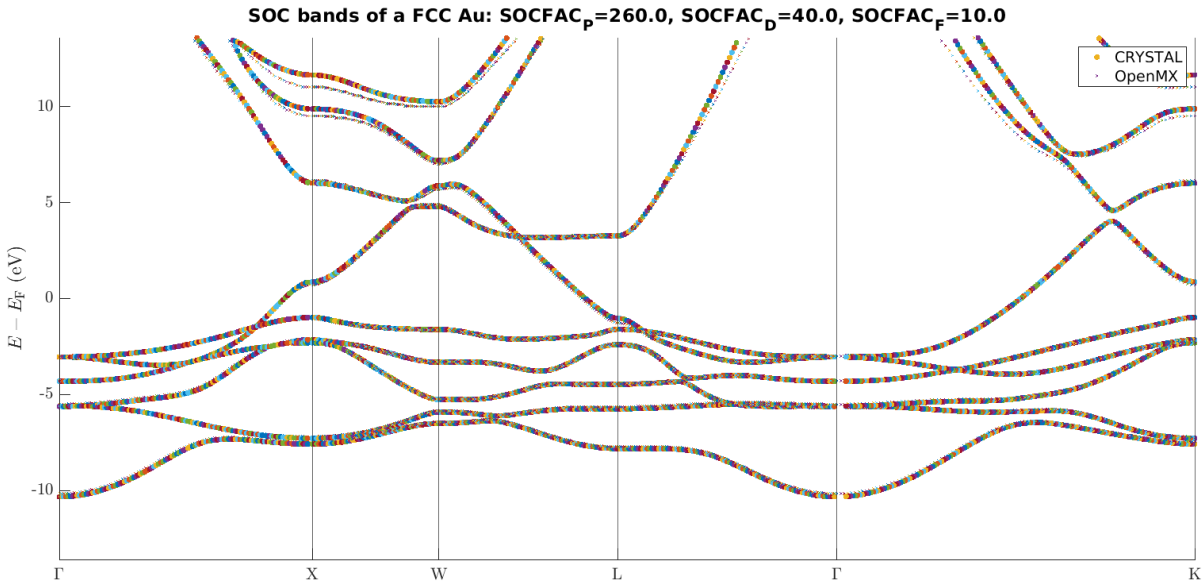

Figure 1. SOC-corrected bands for face-centred cubic Au obtained using the basis set and pseudopotential reported in ref. [5] in `CRYSTAL14` (solid markers) and the reference method `OpenMX` (faint crosses).

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References

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