# DFTB parameters for the Periodic Table: part III, Spin-Orbit Coupling

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## ABSTRACT

Spin-orbit coupling (SOC) is crucially important for the correct description of the electronic structure and transport properties of inorganic semiconductors, and for assessing topological properties as in topological insulators. We present a consistent set of SOC parameters for the density-functional based tight-binding (DFTB) method covering the elements throughout the periodic table. The parameters are based on atomic SOC data calculated at the level of density-functional theory (DFT). We tested these parameters for representative systems with significant

SOC, including transition metal dichalcogenide two-dimensional crystals, III-V bulk semiconductors, and topological insulators. Our parameterization opens the door for DFTB-based electronic structure and transport calculations of very large systems, such as twisted van der Waals heterostructures.

# Introduction

Density-functional theory (DFT) has become the quasi-standard for the description of molecules and materials<sup>1,2</sup> due to its satisfactory accuracy and computational scalability. Nonetheless, chemistry and physics of materials are constantly requiring the calculation of systems incorporating thousands of atoms, as for example in proteins, metal-organic frameworks, or in van der Waals heterostructures. One of the most prominent quantum-mechanical methods that is capable to tackle these systems is the density-functional based tight-binding (DFTB) scheme.<sup>3-5</sup> As an approximation to DFT, physical extensions can be implemented in a straightforward fashion, including spin polarization,<sup>6</sup> relativistic corrections such as scalar-relativistic treatment of the core electrons<sup>7</sup> and spin-orbit coupling.<sup>6</sup> The applicability of DFTB relies on the availability of accurate and transferable parameters. We have reported parameters throughout the periodic table to calculate electronic structures,<sup>8</sup> and also energies and forces,<sup>9</sup> albeit the latter are subject to larger error bars. Here, we focus on the extension of DFTB to include spin-orbit coupling (SOC), for which we provide parameters for the atoms throughout the periodic table. This will allow for electronic structure calculations of a large variety of systems at low computational cost.

SOC is a relativistic term originating intrinsically from the solution of Dirac equation, the relativistic analogue of the non-relativistic Schrödinger equation. A common approach to account for relativity as add-on to the Schrödinger equation is to apply first scalar relativistic

corrections to the inertial mass of the electron through pseudopotentials or other approaches, such as in zeroth order regular approximation (ZORA),<sup>10,11</sup> followed by including SOC by coupling the spin of the electron with the magnetic field in the reference frame of the electron, known as L-S coupling model. In the present work, we used QUASINANO2013 parameters for DFTB, which include scalar relativistic effects through ZORA, while we account for SOC effects with the L-S coupling model through calculated SOC parameters.

The electronic states of periodic structures are typically depicted in reciprocal space as band structures. While SOC typically is a small perturbation, it can play an important role in reshaping the band structure, especially near the fermi level in 3D semiconductors, for example GaAs, InSb, and ZnSe.<sup>12</sup> The SOC-imposed band splittings can be as large as 1 eV, and thus strongly affect the electronic properties of the materials, including their charge carrier mobility and transport properties. Transition metal dichalcogenides (TMDCs) are 2D materials, where SOC effects make valleytronic and spintronic applications possible. MoS<sub>2</sub> monolayer shows large SOC,<sup>13</sup> which vanishes in bilayers because of inversion symmetry,<sup>14</sup> but can be re-introduced by symmetry breaking imposed by applying small external electric fields.<sup>14–16</sup> Hence, a correct theoretical description of SOC is pivotal to analyze the electronic structure of TMDC 2D crystals. In topological insulators (TIs) SOC lies at the origin of the physical phenomenon and must be considered in their theoretical description.<sup>17–19</sup>

Hence, SOC is a crucial physical effect necessary to for the correct description of various materials properties. SOC approximations to DFTB have been proposed and successfully utilized earlier.<sup>20</sup> As further advantage, the computational cost of SOC-corrected DFTB does not exceed that of a non-relativistic spin-polarized DFTB calculation. However, for most elements there are no DFTB parameters including SOC available.

Therefore, in the present study we have calculated the spin orbit splitting parameters throughout the periodic table. We tested them on different benchmark materials where the SOC is important, including TMDC 2D crystals, topological insulators, and bulk III-V semiconductors. For those materials, we could directly compare the impact of SOC on the band structures both for DFTB and DFT. We observe excellent agreement between both methods, that is, the error bar of our SOC correction is typically lower than that expected for the band structures.

#### Method

Theoretical background of SCC-DFTB Hamiltonian: A popular DFTB derivation results from the Taylor expansion of the total energy functional in Kohn-Sham DFT.<sup>5,7</sup> The ground state density, n(r), is the sum of reference density,  $n_0(r)$ , and density fluctuations  $\delta n(r)$ . The total energy is then given by:

$$\begin{split} E_{SCC-DFTB} &= \sum_{i}^{occ} \langle \psi_{i} | \hat{H}[n_{0}] | \psi_{i} \rangle - \frac{1}{2} \iint \frac{n_{0} n_{0}'}{|\vec{r} - \vec{r}'|} + E_{XC}(n_{0}) - \int V_{XC}(n_{0}) n_{0} + \frac{1}{2} \sum_{\alpha,\beta}^{N} \frac{Z_{\alpha} Z_{\beta}}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} \\ &+ \frac{1}{2} \iint \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^{2} E_{XC}}{\delta n \delta n'} \right| n_{0} \right) \delta n \delta n' \end{split}$$

Here,  $E_{XC}$  is the exchange correlation energy, N is the total number of atoms,  $\alpha$  and  $\beta$  represent two different atoms. Following the Linear Combination of Atomic Orbitals (LCAO) ansatz, orbital  $\psi_i$  is expanded in the minimal basis set

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}$$

and only the valence electrons are considered. The atomic orbitals  $\phi_{\mu}$  are calculated employing DFT calculations of atoms subject to a harmonic confinement potential. The Hamiltonian matrix  $H^0_{\mu\nu}$  is given within the LCAO scheme as a two-center approximation to the Hamiltonian  $\hat{H}[n_0]$ ;

$$H^{0}_{\mu\nu} = \langle \phi_{\mu} | \widehat{H}[n_{0}] | \phi_{\nu} \rangle$$
$$H^{0}_{\mu\nu} = \left\langle \phi_{\mu} \left| -\frac{1}{2} \nabla^{2} + V[\rho_{A} + \rho_{B}] \right| \phi_{\nu} \right\rangle$$
$$\mu \in A, \nu \in B$$

Here  $\mu$  and  $\nu$  are the atomic orbitals of atoms *A* and *B* respectively, and  $\rho_A$  and  $\rho_B$  are the atomic densities of atoms *A* and *B* respectively. Charge fluctuations are accounted within the self-consistent charge (SCC) approach:<sup>5</sup>

$$H_{\mu\nu} = H_{\mu\nu}^{0} + H_{\mu\nu}^{2} \text{ with}$$
$$H_{\mu\nu}^{2} = \frac{S_{\mu\nu}}{2} \sum_{C}^{N} (\gamma_{BC}^{h} + \gamma_{AC}^{h}) \Delta q_{C}$$

Here,  $S_{\mu\nu}$  is the overlap matrix and  $\Delta q_c$  is the charge fluctuation of atom *C* with respect to the neutral atom.  $\gamma_{AB}^h$  is the modified interaction of two different atoms *A* and *B* given as:

$$\gamma_{AB}^{h} = \iint \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{XC}}{\delta n \delta n'} \right| n_0 \right) \frac{F_{00}^{A} (|\vec{r} - \vec{R}_A|) F_{00}^{B} (|\vec{r}' - \vec{R}_B|)}{4\pi}$$

Here,  $F_{ml}^{\alpha}$  denotes the normalized radial dependence of the density fluctuation on atom A for the corresponding angular momentum. Expansion of SCC-DFTB with respect to spinfluctuations leads to spin-polarized Hamiltonian expression:

$$H_{\mu\nu}^{spin\pm} = \pm \frac{S_{\mu\nu}}{2} \left( \sum_{l'' \in A} W_{All''} \Delta p_{Al''} + \sum_{l'' \in B} W_{Bll''} \Delta p_{Bl''} \right)$$
$$\mu \in l \in A, \nu \in l' \in B$$

Here  $\mu$  and  $\nu$  are atomic orbitals with angular quantum number l and l' for atoms A and B respectively in two center approximation.  $\Delta p_{Al''}$  is the Mulliken population differences for up and down spin for angular momentum shell l'' at atom A.  $W_{All''}$  is an atomic constant approximating the second derivative of  $E_{XC}(\rho, m)$ , m is the magnetization density as difference of densities of spin up and spin down electrons. Final Hamiltonian  $H_{\mu\nu}$  without spin orbit coupling is as follows:

$$\begin{split} H_{\mu\nu} &= H_{\mu\nu}^{0} + H_{\mu\nu}^{2} + H_{\mu\nu}^{spin\pm} + H_{\mu\nu}^{\hat{L}*\hat{S}} \\ H_{\mu\nu} &= \left\langle \phi_{\mu} \left| -\frac{1}{2} \nabla^{2} + V[\rho_{A} + \rho_{B}] \right| \phi_{\nu} \right\rangle + \frac{S_{\mu\nu}}{2} \sum_{c}^{N} (\gamma_{Bc}^{h} + \gamma_{Ac}^{h}) \Delta q_{c} \\ &\pm \frac{S_{\mu\nu}}{2} \left( \sum_{l'' \in A} W_{All''} \Delta p_{Al''} + \sum_{l'' \in B} W_{Bll''} \Delta p_{Bl''} \right) \end{split}$$

Writing the wave function of the systems as two-component spinors instead of scalar wavefunctions, the total electronic and magnetization density can be given as the linear combination of the Pauli matrices:

$$\vec{n}(\vec{r}) = \sum_{i}^{N} n_{i} \begin{pmatrix} \psi_{i}^{\alpha} \\ \psi_{i}^{\beta} \end{pmatrix}^{*} \begin{pmatrix} \psi_{i}^{\alpha} \\ \psi_{i}^{\beta} \end{pmatrix}$$
$$= n(\vec{r}) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + m^{x}(\vec{r}) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + m^{y}(\vec{r}) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + m^{z}(\vec{r}) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

A straightforward modification of the spin independent Mulliken analysis for spinor wavefunction is given as:

$$\begin{aligned} q_{\mu}^{AB} &= \sum_{i} \sum_{\nu} n_{i} S_{\mu\nu} c_{i\mu}^{\alpha *} c_{i\nu}^{\beta} \\ &= q_{\mu} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + p_{\mu}^{x} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + p_{\mu}^{y} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + p_{\mu}^{z} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned}$$

Here  $c_{i\mu}^{\alpha}$  and  $c_{i\nu}^{\beta}$  are wavefunction coefficients. The density becomes quaternion-like spinor with a vectorial spin and leads to the non-collinear Hamiltonian as:

$$\begin{split} H_{\mu\nu} &= \left\langle \phi_{\mu} \left| -\frac{1}{2} \nabla^{2} + V[\rho_{A} + \rho_{B}] \right| \phi_{\nu} \right\rangle + \frac{S_{\mu\nu}}{2} \sum_{c}^{N} (\gamma_{Bc}^{h} + \gamma_{Ac}^{h}) \Delta q_{c} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ & \pm \frac{S_{\mu\nu}}{2} \left( \sum_{l' \in A} W_{All''} \begin{pmatrix} p_{Al''}^{z} & p_{Al''}^{y} - p_{Al''}^{z} \\ p_{Al''}^{y} + p_{Al''}^{x} & -p_{Al''}^{z} \end{pmatrix} \\ & + \sum_{l' \in B} W_{Bll''} \begin{pmatrix} p_{Bl''}^{z} & p_{Bl''}^{y} - p_{Bl''}^{z} \\ p_{Bl''}^{y} + p_{Bl''}^{x} & -p_{Bl''}^{z} \end{pmatrix} \end{split}$$

With a secular equation:

$$\sum_{\nu} \begin{pmatrix} c_{\nu i}^{\alpha} \\ c_{\nu i}^{\beta} \end{pmatrix} \begin{bmatrix} \begin{pmatrix} \widehat{H}_{\mu\nu}^{\alpha\alpha} & \widehat{H}_{\mu\nu}^{\beta\alpha} \\ \widehat{H}_{\mu\nu}^{\alpha\beta} & \widehat{H}_{\mu\nu}^{\beta\beta} \end{pmatrix} - \varepsilon_i S_{\mu\nu} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{bmatrix} = 0$$

Addition of SOC to the spin-polarized SCC-DFTB Hamiltonian in LS coupling model gives the Hamiltonian expression as:

$$\hat{L} * \hat{S} = \frac{1}{2} \begin{pmatrix} \hat{L}_{Z} & \hat{L}_{-} \\ \hat{L}_{+} & -\hat{L}_{Z} \end{pmatrix}$$
$$\hat{H}^{SO} = \varepsilon (\hat{L} * \hat{S})$$

$$\widehat{H}_{\mu\nu}^{\widehat{L}*\widehat{S}} = \frac{S_{\mu\nu}}{2} \left[ \epsilon_{\mu} \begin{pmatrix} \widehat{L}_{Z} & \widehat{L}_{-} \\ \widehat{L}_{+} & -\widehat{L}_{Z} \end{pmatrix} + \epsilon_{\nu} \begin{pmatrix} \widehat{L}_{Z} & \widehat{L}_{-} \\ \widehat{L}_{+} & -\widehat{L}_{Z} \end{pmatrix} \right]$$

 $\mu \in l \in A, v \in l' \in B$ , where  $\epsilon$  is the spin-orbit coupling parameter,  $\hat{L}$  is the angular momentum operator and  $\hat{S}$  is spin operator.  $\hat{H}^{SO}$  is the Hamiltonian matrix including spin orbit coupling contributions in on site approximation, while  $\hat{H}_{\mu\nu}^{\hat{L}*\hat{S}}$  is the hamiltonian matrix for dual spin orbit coupling.<sup>6</sup> Final Hamiltonian matrix including spin-orbit coupling is given as:

$$\begin{split} H_{\mu\nu} &= \left\langle \phi_{\mu} \left| -\frac{1}{2} \nabla^{2} + V[\rho_{A} + \rho_{B}] \right| \phi_{\nu} \right\rangle + \frac{S_{\mu\nu}}{2} \sum_{C}^{N} (\gamma_{BC}^{h} + \gamma_{AC}^{h}) \Delta q_{C} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ & \pm \frac{S_{\mu\nu}}{2} \left( \sum_{l'' \in A} W_{All''} \begin{pmatrix} p_{Al''}^{z} & p_{Al''}^{y} - p_{Al''}^{z} \\ p_{Al''}^{y} + p_{Al''}^{x} & -p_{Al''}^{z} \end{pmatrix} \\ & + \sum_{l'' \in B} W_{Bll''} \begin{pmatrix} p_{Bl''}^{z} & p_{Bl''}^{y} & p_{AB}^{y} - p_{Bl''}^{x} \\ p_{Bl''}^{y} + p_{Bl''}^{z} & -p_{Bl''}^{z} \end{pmatrix} \\ & + \frac{S_{\mu\nu}}{2} \left[ \epsilon_{\mu} \begin{pmatrix} \hat{L}_{Z} & \hat{L}_{-} \\ \hat{L}_{+} & -\hat{L}_{Z} \end{pmatrix} + \epsilon_{\nu} \begin{pmatrix} \hat{L}_{Z} & \hat{L}_{-} \\ \hat{L}_{+} & -\hat{L}_{Z} \end{pmatrix} \right] \end{split}$$

**Calculation of SOC Parameters:** We have calculated the SOC parameters for free atoms employing AMS-BAND<sup>21</sup> software with two component relativistic corrections at SOC-ZORA level and then renormalized as outlined below. As in the calculation of the QUASINANO2013 parameter set, GGA-PBE<sup>22</sup> exchange correlational functional, and scalar ZORA<sup>10,11</sup> (zeroth order regular approximation) were used. Parameters throughout the periodic table were calculated with TZP basis sets in all electron approach. All elements are in their ground state atomic configuration.

Dirac equation is a well-established quantum mechanical theory. In the non-relativistic limit up to  $1/c^2$ , and in the static spherical potential, the spin-orbit energy can be given as:

$$H_{DIRAC-SOC} = -\frac{e\hbar}{4m^2c^2}\sigma \cdot [E \times p]$$

Where  $\sigma$  is the Pauli matric, *E* is the electric field of the nucleus and *p* is the momentum of the electron. Substituting the electrical field *E* with potential U(r), and rearranging  $\sigma$  with *S*, spin of the particle, and using the Bohr magneton  $\mu_B$ ; spin-orbit energy can be written as:

$$\Delta H_{DIRAC-SOC} = \frac{\mu_B}{\hbar m_e e c^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} L * S$$

Classically, the spin-orbit coupling potential consists of two contributions. The first one is Larmor interaction energy, which stems from the interaction of the magnetic moment of the electron with the magnetic field of the nucleus in the reference frame of electron. Larmor energy  $\Delta H_L$  is given as:

$$\Delta H_L = \frac{2\mu_B}{\hbar m_e ec^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} L * S$$

Here  $\mu_B$  is Bohr magneton and U(r) is spherical potential. In the classical picture, Larmor energy should account for the SOC energy, but it is two-fold larger than the SOC calculated from the Dirac equation to the order of  $1/c^2$ , non-relativistic limit in the quantum mechanical picture. The second contribution is Thomas precession correction for the electron's curved trajectory. It accounts for Thomas correction energy,  $\Delta H_T$  which reduces Larmor energy by two-fold and matches the SOC energy from the Dirac equation,  $\Delta H_{DIRAC-SOC}$ . Thomas precession is a relativistic correction and connects the angular velocity of the spin of a particle to the angular velocity of orbital motion. Here,  $\Omega_T$  is the Thomas precession rate and Lorentz factor  $\gamma$  is a relativistic term quantifying the effect of the velocity of the particle on the measurement of time, space, and other physical properties.

$$\gamma = \sqrt{1 - \frac{v^2}{c^2}}$$
$$\Omega_T = -\omega(\gamma - 1)$$
$$\Delta H_T = \Omega_T * S$$
$$\Delta H_T = -\frac{\mu_B}{\hbar m_e e c^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} L * S$$

Here, Thomas precession factor reduces the Larmor energy by half because of the assumption that non-relativistic limit  $\gamma = 1$  for electron's velocity v << c, where c is the speed of light. This approach is known as Thomas half, and only considers Thomas correction in the non-relativistic limit. In our approach we have used Thomas correction in its original form which considers Lorentz factor  $\gamma$  for the relativistic treatment in the above-mentioned Thomas precession. This additional precession originating from Lorentz factor approaches the non-relativistic limit for light elements and for the heavier elements adds the relativistic treatment. This approach results in decrement of Larmor energy by a factor different than half and gives  $\Delta H_T$  as:

$$\Delta H_T = -\left(\frac{2\gamma^3}{\gamma+1}\right)\frac{\mu_B}{\hbar m_e ec^2}\frac{1}{r}\frac{\partial U(r)}{\partial r}L * S$$

In the non-relativistic limit of light atoms, where  $\gamma = 1$ , the equation gives the previous equation of the Thomas Half approach. Spin-Orbit potential,  $\Delta H$  in terms of  $\Delta H_T$  and  $\Delta H_L$  can be given as:

$$\Delta H = \Delta H_T + \Delta H_L = \left(2 - \frac{2\gamma^3}{\gamma + 1}\right) \frac{\mu_B}{\hbar m_e ec^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} L * S$$

Where 
$$\gamma = \sqrt[2]{1 - \left(\frac{Z}{n\alpha}\right)^2}$$
 derived by using  $\frac{v}{c} = \frac{Z}{n\alpha}$  in  $\gamma = \sqrt{1 - \frac{v^2}{c^2}}$ 

Here, Z is the atomic number of the atom, n is the principal quantum number, and  $\alpha$  is the fine structure constant or Sommerfeld constant.

We performed a renormalization of the parameters calculated above with the angular quantum number of the respective orbital. The renormalization with angular momentum l stems from the admixture of higher angular momentum states in top of the valence bands.<sup>23,24</sup> This resulted in spin-orbit coupling parameter expression given as:

$$\epsilon = \frac{2\Delta}{l} \left( 1 - \frac{\gamma^3}{\gamma + 1} \right)$$

Here  $\Delta$  is the SO splitting from atomic calculations in BAND with SOC relativistic corrections at ZORA level, two-component relativistic approximation to Dirac equation; and *l* is the angular quantum number for respective shells, and  $\epsilon$  is the renormalized spin-orbit coupling constant. Table 1 contains the calculated SOC parameters throughout the periodic table. The spin-orbit coupling Hamiltonian matrix elements were calculated with the parameters in the LS coupling model and used variationally in the self-consistent field optimization.

 Table 1. Renormalized Spin-orbit coupling parameters calculated at GGA-PBE/SOC-ZORA/AE

 theory level. All values are in milli-Hartrees.

	ε <b>(p)</b>	ε <b>(d)</b>	ε <b>(f)</b>		ε <b>(p)</b>	ε( <b>d</b> )	ε <b>(f)</b>		ε <b>(p)</b>	ε <b>(d)</b>	ε <b>(f)</b>		ε <b>(p</b> )	ε <b>(d)</b>	ε <b>(f)</b>
Н		—	_	Ga	3.93	—	_	Pm	112.6	3.83	5.38	Pa	207.12	7.24	61.41
He		_	_	Ge	6.32	_		Sm	121.0	3.98	6.11	U	244.96	7.68	73.13

Li				As	9.21			Eu	129.7	4.13	6.89	Np			
Be	_	_		Se	12.63	_	_	Gd	138.8	4.27	7.71	Pu	_	_	_
В	0.12			Br	16.65	_	_	Tb	148.4	4.40	8.59	Am	_	_	_
С	0.31			Kr	21.30			Dy	158.3	4.52	9.53	Cm	_	_	
N	0.68			Rb	29.33			Но	168.7	4.63	10.53	Bk	_	_	
0	1.29			Sr	38.61			Er	179.6	4.73	11.58	Cf	_	_	
F	2.24			Y	48.24	1.44		Tm	191.0	4.82	12.71	Es	_	_	
Ne	3.62			Zr	58.69	2.13		Yb	203.0	4.90	13.89	Fm	_		
Na	6.23			Nb	69.15	2.55		Lu	215.5	4.97		Md	_	_	
Mg	9.99			Мо	81.64	3.35		Hf	242.8	7.01		No	_	_	
Al	0.57	_		Тс	96.65	4.69	_	Та	272.7	9.11		Lr	551.55	9.33	_
Si	1.11	_		Ru	110.5	5.26	_	W	305.2	11.33		Rf	612.09	13.07	_
Р	1.87	_		Rh	127.0	6.39	_	Re	340.4	13.69	_	Db	677.68	16.73	_
S	2.92	_		Pd	143.8	7.07	_	Os	378.2	16.20	_	Sg	748.40	20.47	_
Cl	4.30	_		Ag	164.7	9.02	_	Ir	418.8	18.89		Bh	824.43	24.35	_
Ar	6.08			Cd	188.1	11.25	_	Pt	458.7	20.43		Hs	905.99	28.38	_
K	9.20			In	10.32			Au	505.0	23.40		Mt	993.39	33.81	
Ca	13.19			Sn	14.69			Hg	558.4	28.07		Ds	1087.0	37.02	
Sc	17.46	0.52	_	Sb	20.05			Tl	32.76			Rg	1187.1	41.64	
Ti	22.45	0.79		Te	26.08			Pb	46.13			Cn	1294.1	48.62	
V	28.28	1.12		Ι	32.82			Bi	60.46			Nh	93.31	_	
Cr	34.44	1.31		Xe	40.33			Ро	75.98			Fl	125.51	_	
Mn	42.88	1.99		Cs	53.23			At	92.82			Мс	159.60	_	_

Fe	51.86	2.56	—	Ba	67.51			Rn	111.1			Lv	196.28	_	
Co	62.09	3.22	—	La	81.52	3.06	2.88	Fr	141.9	—		Ts	235.98	_	—
Ni	72.77	3.64	_	Ce	89.01	1.96	3.46	Ra	175.0			Og	278.99	_	—
Cu	85.78	4.49	_	Pr	96.63	3.47	4.06	Ac	141.3	5.86					
Zn	101.5	5.90	_	Nd	104.5	3.66	4.70	Th	174.2	8.14	50.37				

#### **Computational Details of the DFT benchmark calculations**

We optimized geometries at periodic DFT level (PBE functional) as implemented in AMS-BAND, in conjugation with scalar relativistic corrections at the ZORA level. All electron approach was used with TZP basis set at normal numerical quality. All DFTB calculations were performed within the SCC-DFTB formalism as implemented in DFTB+. QUASINANO2013 Slater-Koster parameters were used for band structure calculations. These parameters were calculated with scalar ZORA approach and already account for scalar relativistic effects.<sup>10,11</sup> It should be noted that the objective of QUASINANO2013 parameter generation was to match PBE band structures of monatomic materials, including the conduction band (both without including SOC).8 SOC effects were accounted in DFTB calculations through SOC parameters as given in Table 1. To compare the results with their corresponding PBE-DFT references, AMS-BAND software was used with same theory level as in geometry optimization, but with SOC ZORA to consider the SOC contributions. All band structure calculations were done using a Monkhorst Pack k-space with 4\*4\*2 grid points for 3D semiconductors and 4\*4\*1 for the 2D TMDCs and topological insulators. For plotting band structures, kLine method was used in DFTB+ after initial single point calculations with proper k-sampling as mentioned above. For band structure calculations at DFT level, interpolation of  $\Delta K$  was set to 0.1 Bohr<sup>-1</sup>.

# **Benchmarking Spin-Orbit Coupling Parameters**

# **III-V Bulk Semiconductor**

GaAs is a 3D semiconductor with pronounced SOC-induced band splittings, most prominently close to the valence band maximum (VBM). Fig 1. depicts the resemblances between DFTB and DFT results with and without SOC. DFTB agrees well for the valence band, but overestimates (as known for other systems) the band gap (which is underestimated in PBE, but we will not discuss this point here). The SOC-triggered band splitting at the VBM is perfectly reproduced by SOC-SCC-DFTB.





**Fig 1**. Band Structure of 3D GaAs with and without spin orbit coupling at DFT and DFTB level. Fermi energy has been shifted to top of the valence band.

We then calculated the SOC splittings for a range of other III-V semiconductors at the DFTB and DFT level, which show the expected increase when going to heavier elements (Figure 2). The excellent agreement between DFTB and other calculations and experiment is evident from the numerical slitting values at the high symmetry points of the Brillouin zone that are listed in Table 2.



(a)



**Fig 2**. Band structure of III-V bulk semiconductors calculated at DFTB level, with and without the incorporation of spin orbit coupling. (a) GaAs (b) InSb (c) ZnSe. Conventions as in Figure 1. Fermi energy has been shifted to the top of the valence band.

**Table 2**. Spin-orbit splitting for III-V bulk semiconductors calculated at DFTB. All values are in eV.  $\Delta(\Gamma)$  and  $\Delta(L)$  are the SO splitting of the valence band at  $\Gamma$  and L k-point.  $\Delta(\Gamma')$  and  $\Delta(L')$ 

are the splitting of the conduction band at  $\Gamma$  and L point.  $\sigma$  is the standard deviation (SD) of SO splitting from reference values.

	$\Delta \left( \Gamma  ight)$				$\Delta(\Gamma')$				Δ(L)				Δ(L')				
	DFTB (This work)	XPS <sup>23</sup> /ER <sup>25</sup>	PBE (This work)	σ (SD)	DFTB (This work)	ROPM <sup>26</sup> / ER <sup>27</sup>	PBE (This work)	σ (SD)	DFTB (This work)	XPS <sup>23</sup> /ER <sup>25</sup>	PBE (This work)	σ (SD)	DFTB (This work)	ROPM <sup>26</sup> / ER <sup>27</sup>	PBE (This work)	σ (SD)	
GaAs	0.355	0.340 XPS	0.338	0.01	0.181	0.260 ROPM	0.187	0.04	0.216	0.230 XPS	0.208	0.01	0.139	0.110 ROPM	0.085	0.03	
InSb	0.742	0.810 XPS	0.750	0.04		_			0.461	0.500 XPS	0.471	0.02			_	_	
ZnSe	0.381	0.450 ER	0.383	0.04		_			0.211	0.300 ER	0.225	0.05			_		
Si	0.050	0.044 XPS	0.050	0.01					0.030	0.029 XPS	0.032	0.01			_		
Ge	0.258	0.290 XPS	0.290	0.02	0.258	0.200 ER	0.214	0.03	0.176	0.200 XPS	0.186	0.01	0.169	0.266 ER	0.096	0.08	

\*ER stands for Electroreflectance Spectra

\*\*ROPM stands for Relativistic Orthogonalized Planewave Model

§XPS (X-Ray Photoemission Spectroscopy)

# **Transition Metal Dichalcogenide 2D Crystals**

We chose  $TX_2$  monolayer, where T=W, Mo and X=S, Se, as reference structures for TMDC two dimensional crystals. In the monolayer form, these materials show SO splitting between 140-500 meV,<sup>16,28</sup> which vanishes in bilayer form due to the presence of inversion symmetry.<sup>14</sup> Table 3 lists the SO splittings for the reference TMDCs.

**Table 3**. Spin-Orbit splitting for TMDC two-dimensional crystals (monolayers),  $TX_2$  (T=W, Mo and X= S, Se), calculated at DFTB level. All values are in eV. The values are calculated at the direct band gap position in the Brillouin zone at the K point.

Material	DFTB	TB-mBJ <sup>15</sup>	PBE <sup>15</sup>	PBE <sup>28</sup>	PBE <sup>29</sup>	PBE
	(This work)	(ADF/BAND/	(ADF/BAND/	(WIEN2K/	(Q.ESPRESSO	(This
		TZP, TZ2P)	TZP, TZ2P)	FLAPW)	/VAN)	work)
MoS <sub>2</sub>	0.153	0.147	0.147	0.148	0.150	0.149
WS <sub>2</sub>	0.448	0.395	0.419	0.426	0.431	0.418
MoSe <sub>2</sub>	0.185	0.176	0.180	0.183	0.188	0.181
WSe <sub>2</sub>	0.474	0.428	0.449	0.456	0.473	0.444

As expected from symmetry,<sup>15,16</sup> DFTB yields no SO splitting in the TMDC bilayers (Figure 3). All SO splitting values for all TMDC monolayers considered here show an excellent match with other available references. Zhu *et al.* obtained the SO splitting of 0.148, 0.183, 0.426, and 0.456 eV for MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> respectively at K point of VBM using the full-potential linearized augmented plane wave approach at PBE level.<sup>28</sup> Using the plane wave approach with ultrasoft pseudopotentials at PBE level Cheng *et al.* obtained SO splitting of 0.150, 0.188, 0.431, and 0.473 for MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> respectively.<sup>29</sup> Zibouche *et al.* calculated SO splittings at K point of VBM at PBE level as well as with TB-mBJ potential, using slater type basis functions (table 3).<sup>15</sup>





**Fig 3**. Band structures of (TMDCs) two dimensional crystals, MX2 (M=Mo, W, X=S, Se) calculated at the DFTB level, with and without the incorporation of spin-orbit coupling. Fermi energy has been shifted to the top of the valence band.

# **Topological Insulators**

As final test we tested if SOC results in the well-known band inversion known for 2D topological insulators (TIs), as reported, for example, for methyl functionalized Bi(111), Sb(111), and Pb(111) bilayers.<sup>30</sup> In these three systems, large SO splittings and gap openings at the Dirac point have been found.<sup>30</sup>



**Fig 3**. Band structures of Me functionalized Bi(111), Pb(111), and Sb Bilayers(111) topological insulators at the DFTB level, with and without the incorporation of spin orbit coupling parameters.

The SOC-induced band gap openings known from the DFT calculations of Ma *et al.* are reproduced for all three 2D TI systems, as shown in Figure 3, where the band gap splitting is indicated.<sup>30</sup> SOC induced band gap openings in Me-Bi, Me-Sb, and Me-Pb are 0.858 eV, 0.418 eV, and 1.048 eV, respectively, and thus in close accordance with the previous findings of 0.934 eV, 0.386 eV, and 0.964 eV.<sup>30</sup>

# Conclusions

We have discussed the parameterization strategy of the spin orbit coupling for the framework of density functional based tight binding method and calculated parameters for the elements throughout the periodic table. We tested the SOC-SCC-DFTB formalism on the reference structures including III-V semiconductors, 2D TMDCs, and 2D topological insulators. None of these systems have been used either for generating the utilized QUASINANO2013 parameters nor for the calculation of the SOC parameters. The resulting SO splittings are in close accordance with DFT-based reference calculations, with deviations smaller than those that are expected for DFTB band structures. This demonstrates excellent transferability and raises confidence that these parameters will be very useful for a wide range of applications where SOC is important. Examples include topological insulators in all dimensionalities, the calculation of charge carrier mobilities and the performance of electronic materials.

With this work, it is now possible to incorporate SOC in all calculations without additional computational costs compared to the spin-polarized SCC-DFTB approach. This work also extends the parameters availability throughout the periodic table which was limited to a few p- and d-block elements in the works of Chadi *et al.*<sup>12</sup>

As DFTB is a well-defined approximation to DFT, extensions to the Hamitonian are system independent and transferable within different parameterizations. Therefore, the presented parameters work well for various DFTB parameterizations as found at dftb.org and they have been tested in DFTB+ software.

Our parameters are available at GitHub for incorporation of spin-orbit coupling for DFTB implementations beyond DFTB+ (https://github.com/gajh494c/SOC-DFTB).

### ASSOCIATED CONTENT

**Supporting Information**. Detailed information on the Spin-Orbit coupling parameters, and geometric parameters of all crystal structures considered in this work. This material is available free of charge.

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#### Notes

The authors declare no competing financial interest.

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