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Spin Orbit coupling implementation in DFTB/GFN-xTB

SCM // Amsterdam, Jul 23, 2024

From DFT to DFTB

Kohn-Sham equations $E = E[\rho(\mathbf{r})]$

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- $E^0[\rho_0] = -\frac{1}{2}\int\int \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' - \int V^{xc}[\rho_0]\rho_0(\mathbf{r})d\mathbf{r} + E_{\text{xc}}[\rho_0] + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{R_{AB}}$
- $E_1[\rho_0, \delta\rho] = \sum_i^{\text{occ}} f_i\langle\psi_i| - \frac{1}{2}\nabla^2 + V_{\text{ext}} + \int\frac{\rho_0(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}[\rho_0]|\psi_i\rangle$
- $E^2[\rho_0, \delta\rho^2] = \frac{1}{2}\int\int\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right)\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$

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Non-SCC (?) DFTB (DFTB1)

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$$= \sum_{I<J} V_{IJ}^{\text{rep}}(\mathbf{r}_{IJ}) + \sum_{i}^{\text{occ}} f_i \langle\psi_i|\hat{H}[\rho_0]|\psi_i\rangle + \ldots$$

Phys. Rev. B **51**, 12947 (1995)

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- minimal "pseudo" atomic basis set $\psi_i = \sum_\mu c_{\mu i}\varphi_\mu$
- reference density ρ_0
- tabulated as function of distance

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SCC-DFTB(DFTB2) and DFTB3

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Phys. Rev. B **58**, 7260 (1998)

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$$\Big\downarrow \quad \delta\rho(\mathbf{r}) = \textstyle\sum_I \Delta q_I \delta\rho_I(\mathbf{r})$$

- $E^2[\rho_0, \delta\rho^2] \approx \frac{1}{2} \sum_{IJ} \gamma_{IJ}(R_{IJ}) \Delta q_I \Delta q_J$

SCC-DFTB(DFTB2) and DFTB3

- $E_{\text{DFTB2(3)}} = E_{\text{Non-SCC}} + \frac{1}{2}\sum_{IJ}\gamma_{IJ}(R_{IJ})\Delta q_I \Delta q_J + \frac{1}{3}\sum_{IJ}\Delta q_I^2 \Delta q_J \Gamma_{IJ}$
- $H_{\mu\nu} = H^0_{\mu\nu} + H^2_{\mu\nu}[\gamma^h, \Delta q] + H^3_{\mu\nu}[\Gamma, \Delta q], \quad \mu \in I,\, \nu \in J$
- $q_I = \sum_i f_i \int_{V_I} |\psi_i(\mathbf{r})|^2\, d^3r = \frac{1}{2}\sum_i^{\text{occ}} f_i \sum_{\mu\in I}\sum_\nu \left(c^*_{\mu i} c_{\nu i} S_{\mu\nu} + c^*_{\nu i} c_{\mu i} S_{\nu\mu}\right)$

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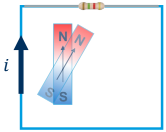
Charges iterated until self consistency has been reached

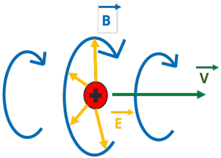
$$q^{(0)} \xrightarrow{H^{(0)}_{\mu\nu}} c^{(0)}_{ij} \rightarrow q^{(1)} \xrightarrow{H^{(1)}_{\mu\nu}} c^{(1)}_{ij}$$

Self-consistent charge (SCC) iteration

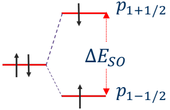
Spin-Orbit Coupling (SOC)



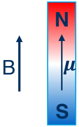
Hans C. Ørsted (1777-1851)



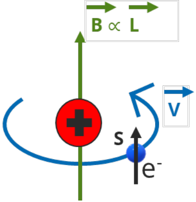
Moving charge creates magnetic field (1820)



$$\Delta E_{SO} = \xi(L \cdot S)$$



$$E = -\boldsymbol{\mu} \cdot \mathbf{B}$$



- SOC hamiltonian in Dirac Equation

$$\hat{H}^{SOC} = -\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot [E_f \times \hat{p}]$$

- Spherical potential & static case

$$\hat{H}^{SOC} = -\frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{\sigma} \cdot [\hat{r} \times \hat{p}]$$

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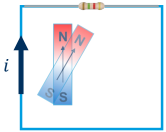

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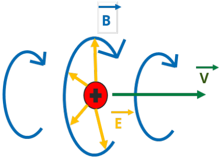

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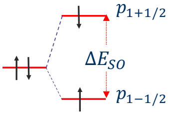

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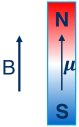

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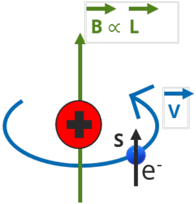

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See *J. Chem. Theory Comput.* **18**, 4472 (2022)

SOC implementation in DFTB

- Single-particle on-site spin-orbit interaction

$$\hat{H}_{SO} = \frac{\zeta}{2}\mathbf{L}\cdot\mathbf{S} = \frac{\zeta}{2}(\hat{L}_x\sigma_x + \hat{L}_y\sigma_y + \hat{L}_z\sigma_z)$$

$$= \frac{\zeta}{2}\begin{pmatrix} \hat{L}_z & \hat{L}_x - i\hat{L}_y \\ \hat{L}_x + i\hat{L}_y & \hat{L}_z \end{pmatrix} = \frac{\zeta}{2}\begin{pmatrix} \hat{L}_z & \hat{L}_- \\ \hat{L}_+ & \hat{L}_z \end{pmatrix}$$

Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

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J. Phys. Chem. A **111**, 5622 (2007)

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  - $\hat{L}_z|Y_l^{\pm m}\rangle = \pm ml|Y_l^{\pm m}\rangle$, $\quad \hat{L}_\pm|Y_l^{\pm m}\rangle = \sqrt{l(l+1) - m(m\pm 1)}|Y_l^{\pm m}\rangle$
  - $\varphi_\mu(\mathbf{r} - \mathbf{R}_I) = R_\mu(r)\widetilde{Y}_\mu(\theta,\varphi)(\mu \in I)$, where $\widetilde{Y} \propto Y_{lm} \pm Y_{lm}^*$

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SOC implementation in DFTB

- 2-component spinor wavefunctions

$$\psi_i = \sum_{\mu} \begin{pmatrix} c^{\alpha}_{\mu i} \\ c^{\beta}_{\mu i} \end{pmatrix} \varphi_\mu$$

- Non-collinear Hamiltonian

$$\hat{H} = \left(\hat{H}^0_{\mu\nu} + \hat{H}^2_{\mu\nu} + \hat{H}^3_{\mu\nu}\right) \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \left[\xi^l_I \begin{pmatrix} \hat{L}_z & \hat{L}_- \\ \hat{L}_+ & -\hat{L}_z \end{pmatrix}_l + \xi^{l'}_J \begin{pmatrix} \hat{L}_z & \hat{L}_- \\ \hat{L}_+ & -\hat{L}_z \end{pmatrix}_{l'}\right]$$

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- Secular equation

$$\sum_\mu \begin{pmatrix} H^{\alpha\alpha}_{\mu\nu} - \epsilon_i S_{\mu\nu} & H^{\alpha\beta}_{\mu\nu} \\ H^{\beta\alpha}_{\mu\nu} & H^{\beta\beta}_{\mu\nu} - \epsilon_i S_{\mu\nu} \end{pmatrix} \begin{pmatrix} c^\alpha_{\mu i} \\ c^\beta_{\mu i} \end{pmatrix} = 0, \quad H^{\sigma\sigma'}_{\mu\nu} = \langle \varphi_\mu | \hat{H}^{\sigma\sigma'} | \varphi_\nu \rangle$$

SOC implementation in DFTB

- Density matrix

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} f_i \begin{pmatrix} \psi_i^{\alpha *} \\ \psi_i^{\beta *} \end{pmatrix} \begin{pmatrix} \psi_i^{\alpha} & \psi_i^{\beta} \end{pmatrix} = \begin{pmatrix} \rho^{\alpha\alpha} & \rho^{\alpha\beta} \\ \rho^{\beta\alpha} & \rho^{\beta\beta} \end{pmatrix}$$

$$= n(\mathbf{r}) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + m^x(\mathbf{r})\sigma_x + m^y(\mathbf{r})\sigma_y + m^z(\mathbf{r})\sigma_z$$

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- Electron and magnetization densities

$$n(\mathbf{r}) = \tfrac{1}{2}\,\mathrm{Re}\left(\rho^{\alpha\alpha} + \rho^{\beta\beta}\right), \quad m^z(\mathbf{r}) = \tfrac{1}{2}\,\mathrm{Re}\left(\rho^{\alpha\alpha} - \rho^{\beta\beta}\right)$$

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- Mulliken charges

$$q_\mu = \tfrac{1}{2}\left(q_\mu^{\alpha\alpha} + q_\mu^{\beta\beta}\right), \quad q_\mu^{\sigma\sigma'} = \textstyle\sum_\nu \rho^{\sigma\sigma'} S_{\mu\nu}$$

SOC implementation in DFTB

- Energy : $E_{\mathrm{SO}} = \mathrm{Tr}(\rho H_{\mathrm{SO}})$

$$E_{\mathrm{SO}} = \sum_{\mu\nu} \left[H_{\mathrm{SO}}^{\alpha\alpha} \rho_{\nu\mu}^{\alpha\alpha} + H_{\mathrm{SO}}^{\beta\beta} \rho_{\nu\mu}^{\beta\beta} + 2\,\mathrm{Re}\left(H_{\mathrm{SO}}^{\alpha\beta} \rho_{\nu\mu}^{\alpha\beta} \right) \right]$$

- Forces : $\mathbf{F}_{\mathrm{SO},I} = -\sum_{\sigma\sigma'} \frac{\partial E_{\mathrm{SO}}^{\sigma\sigma'}}{\partial \mathbf{R}_I}$

$$\mathbf{F}_{\mathrm{SO},I} = \sum_{\mu\nu,\mathbf{R}} \left[\sum_{\sigma\sigma'} \rho_{\mu\nu}^{\sigma\sigma'}(\mathbf{R}) \frac{\partial H_{\mathrm{SO}}^{\sigma\sigma'}(\mathbf{R})}{\partial \mathbf{R}_I} - \sum_{\sigma\sigma'} \rho_{\mathrm{SO}}^{\epsilon,\sigma\sigma'}(\mathbf{R}) \frac{\partial S_{\mu\nu}(\mathbf{R})}{\partial \mathbf{R}_I} \right]$$

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  - No explicit contribution

Bi_2	Bond Length (Å)	Frequency (cm^{-1})
w SOC	1.98	1366
w/t SOC	2.02	1336

Table: calculated with GFN1-xTB in AMS/DFTB

SOC implementation in DFTB

- Periodic boundary conditions

$$\phi_\mu^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \varphi_\mu(\mathbf{r} - \mathbf{R})$$

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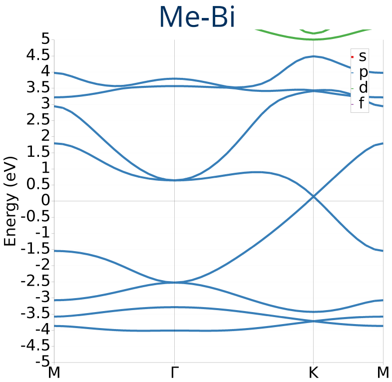
- Fatbands

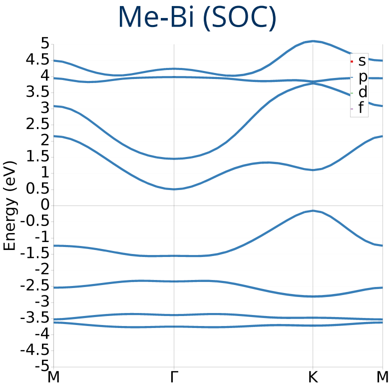
$$n_{i\mathbf{k}}^{\mu} = \sum_{\nu} \left| \langle \psi_{\mu}^{\mathbf{k}} | \phi_{\nu}^{\mathbf{k}} \rangle \right|^2 = \frac{1}{2} \sum_{\nu} \mathrm{Re} \left(c_{\mu i\mathbf{k}}^{\alpha *} c_{\nu i\mathbf{k}}^{\alpha} S_{\mu\nu} + c_{\mu i\mathbf{k}}^{\beta *} c_{\nu i\mathbf{k}}^{\beta} S_{\mu\nu} \right)$$

- Spin texture $S_{i\mathbf{k}} = \langle \psi_{i\mathbf{k}} | \sigma | \psi_{i\mathbf{k}} \rangle$

$$m_{i\mathbf{k}}^{\mu,z} = \frac{1}{2} \sum_{\nu} \mathrm{Re} \left(c_{\mu i\mathbf{k}}^{\alpha *} c_{\nu i\mathbf{k}}^{\alpha} S_{\mu\nu} - c_{\mu i\mathbf{k}}^{\beta *} c_{\nu i\mathbf{k}}^{\beta} S_{\mu\nu} \right)$$

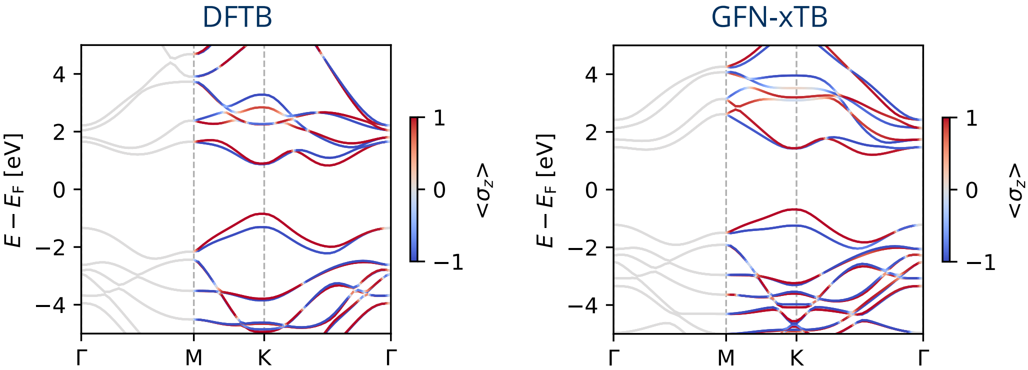
Benchmark calculations





- Me functionalized Bi(111) topological insulators
- QUASINANO2013 Slater-Koster parameters
- Visualized in amsbands

Benchmark calculations



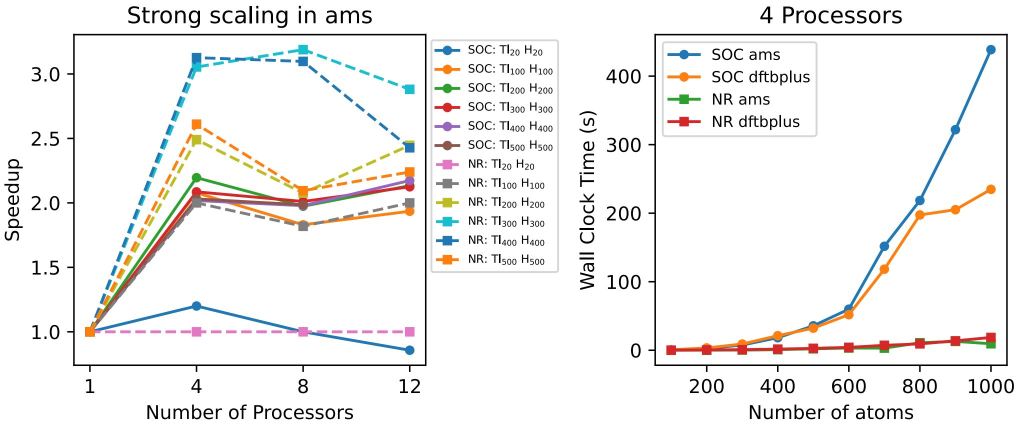
- 2D WS_2 with SOC
- Plotted with python
- Spinor Visualization in amsbands to be done

Benchmark calculations

- H_{SO} is **transferable** among different parameter sets and methods
- Successful benchmarked on close-shell **molecules** and **materials** such as III-V 3D semiconductors, TMDC 2D crystals, topological insulators, with comparison to DFTB+
- **Regression test** on single point calculation, geometry optimization, and frequency calculation

Scalability

TlH chain



THANK YOU

Backup: GFN-xTB

$\psi_i = \sum_\mu c_{\mu i}\varphi_\mu(\zeta, \mathsf{STO} - mG)\mathsf{b}$

$$H_{\mu\nu} = K_{IJ}\frac{1}{2}(k_l + k_{l'})\frac{1}{2}(h_J + h_{J'})S_{\mu\nu}(1 + k_{EN}\Delta E_N^2)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \Pi(R_{I,l'})\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$
$$+\frac{1}{2}S_{\mu\nu}\sum_c\sum_{l''}\left(Y_{IC,l''} + Y_{JC,l''}\right)P^c_{l''}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \frac{1}{2}S_{\mu\nu}(q_I^2 + q_J^2)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$
$$+\frac{1}{2}S_{\mu\nu}\left[\epsilon_\mu\begin{pmatrix}L_z & L_-\\ L_+ & -L_z\end{pmatrix} + \epsilon_v\begin{pmatrix}L_z & L_-\\ L_+ & -L_z\end{pmatrix}\right]$$