Spin Selectivity in Chiral Molecules from relativistic DFT Calculations

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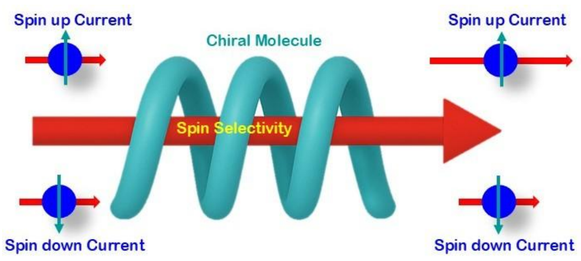
Abstract and Background Theory with Motivations

The Chirality-Induced Spin Selectivity effect, the ability of chiral systems to spin-polarise the currents they are crossed by, has been widely reported since its discovery in 1999. However, a general and comprehensive explanation is still missing. Focusing on carbon-based molecules whose chirality can be tuned by torsion, we investigate spin filtering effects on the transport properties by employing a spin-resolved non-equilibrium Green's function formalism based on fully relativistic density functional theory calculations. We compute, in particular, the chirality of the electronic states and the spin polarization of their conductance in dependence of their energy. We show that non-vanishing integral particles' chirality and spin-polarised conductance emerge naturally at finite torsions, by virtue of the full account of spin-orbit couplings. A large compensation between occupied states of similar energy, which limits the value of the integral quantities, highlights the importance of native structural chirality and of out of equilibrium conditions.

Key Objectives

- ❖ Quantify electronic chirality via the γ^5 operator and its expectation value.
- ❖ Demonstrate intrinsic spin-momentum locking induced purely by structural chirality.
- ❖ Investigate possible links between structural chirality and spin-polarized transport in coherent tunneling.
- ❖ Explore electric-field tunability of electronic chirality, enabling control of spin selectivity.

Chirality, when treated within the fully relativistic Dirac framework, reveals spin selectivity as a fundamental consequence of electron dynamics, not the results of an ad hoc enhancement of spin-orbit coupling.



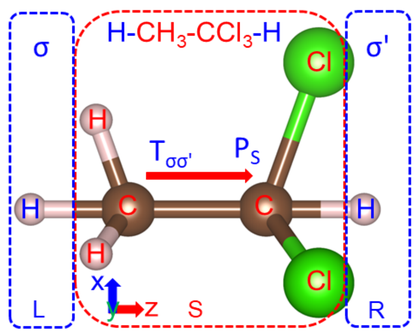
A chiral molecule generating spin-polarized current

Theory & Formalism

- ❖ The Dirac equation is $(i\gamma^\mu\partial_\mu - m)\psi = 0$. where μ = 0,1,2,3 space-time (4×4 γ (gamma) matrices) indices, and ψ is now a four-component (*4C*) Dirac spinor, defines particle's chirality.
- ❖ A fifth one is defined as the product of the others; $\gamma^5 \equiv i\gamma^0\gamma^1\gamma^2\gamma^3$.
- ❖ Chirality density at any spacetime point x can be defined;

$$\chi(x) = \sum_{\mu\vartheta} \psi^*_\mu(x)\gamma^5_{\mu\vartheta}\psi_\vartheta(x).$$

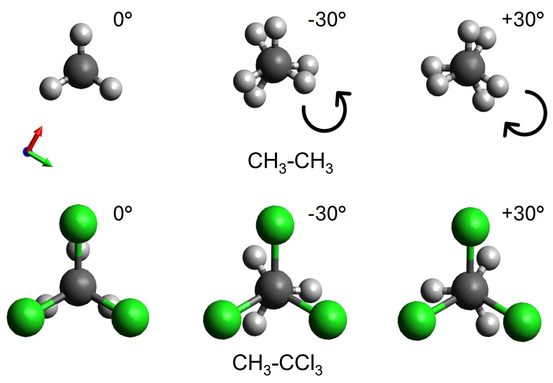
- ❖ In the weak relativistic limit, the *4C* Dirac spinors can be mapped into *2C* Pauli matrices.
- ❖ For electrons subject to voltage V, the current can be calculated as, $I_{\sigma,\sigma'} = \frac{e}{h}\int_{E-\frac{eV}{2}}^{E+\frac{eV}{2}} T^{\sigma,\sigma'}(E)dE$
- ❖ The *T* describes the probability percentage (%) of the transmitted electron computed as, $T^{\sigma,\sigma'} = Tr[\Gamma_L^{\sigma'\sigma'} G^{\sigma\sigma'} \Gamma_R^{\sigma\sigma} (G^{\sigma\sigma'})^\dagger]$. Here, Γ_L and Γ_R are the coupling matrices of left and right lead.
- ❖ $2T = T^{\uparrow\uparrow} + T^{\downarrow\uparrow} + T^{\uparrow\downarrow} + T^{\downarrow\downarrow}$, where, $T^{\uparrow\uparrow}/T^{\downarrow\downarrow}$ spin-conserving, and $T^{\downarrow\uparrow}/T^{\uparrow\downarrow}$ spin-flip.
- ❖ $P_S = \frac{\{T^{\uparrow\uparrow}+T^{\downarrow\uparrow}-T^{\uparrow\downarrow}-T^{\downarrow\downarrow}\}}{2T}$. It is energy-dependent.
- ❖ The spin polarization (P_S) value is a crucial property for CISS.
- ❖ Equilibrium (DIRAC code) & out of equilibrium (Python script).



Two-terminal transport setup Scheme

Equilibrium Studies

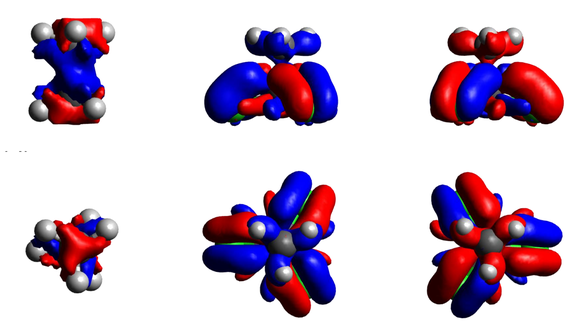
Isolated molecular geometry



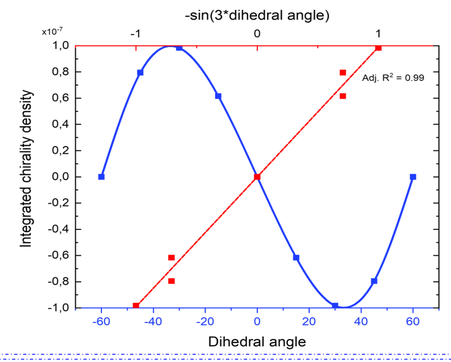
Geometrical chirality

1. Electronic Structure in a Relativistic Framework
   Using the DIRAC code:
   a) 4c or exact two-component (X2C) formalism
   b) Self-consistent inclusion of single-electron SOC
   c) Spinor molecular orbitals
   d) Field-dependent via Electric Field
2. Transport & Out of Equilibrium Workflow
   a) DIRAC generates MO coefficients, eigenvalues, etc.
   b) A Python NEGF post-processing script
   c) Calculation of DOS, energy-resolved T(E) & P_s(E)
   d) Finite-bias transport under non-equilibrium conditions

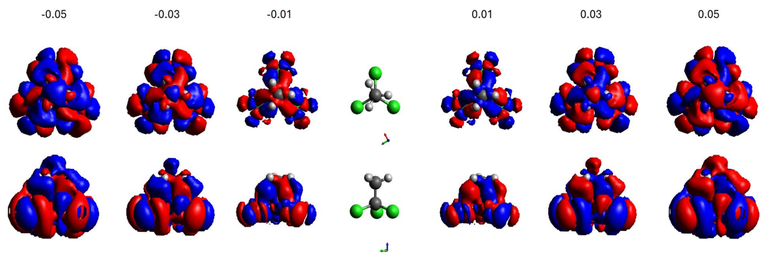
Chirality Density without electric field

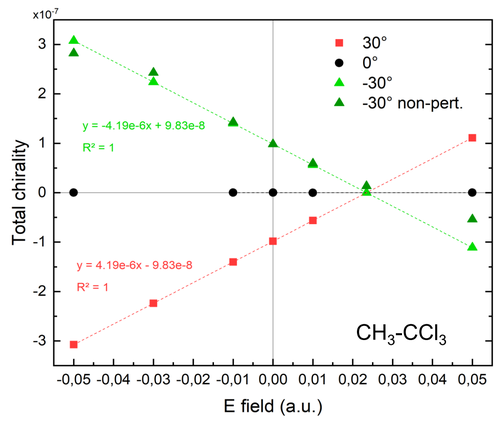


Electronic chirality

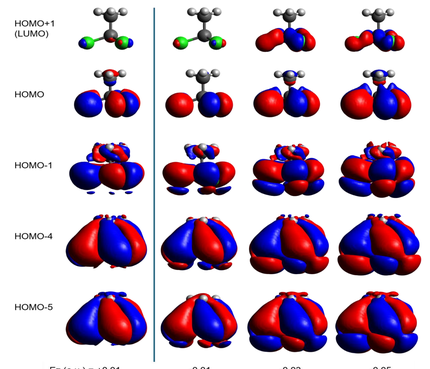


Chirality density in Linear Response field

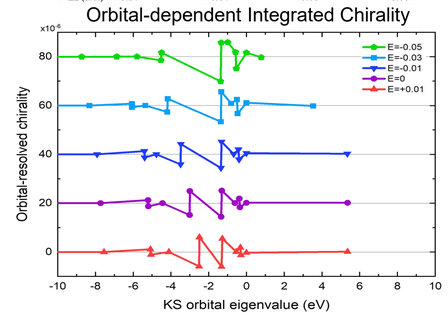




Chirality Properties

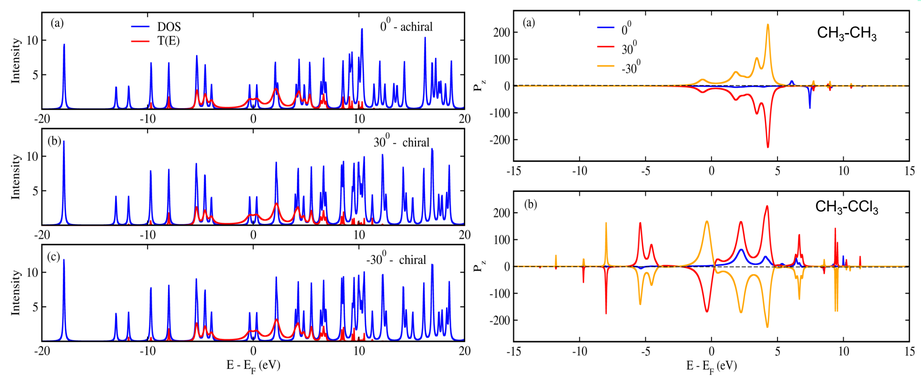


Orbital-dependent Integrated Chirality



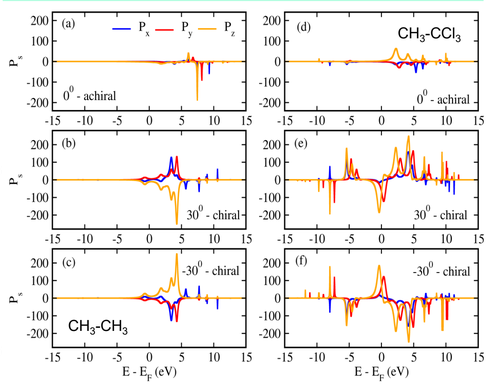
Out of Equilibrium Studies

Transmission Properties without electric Field



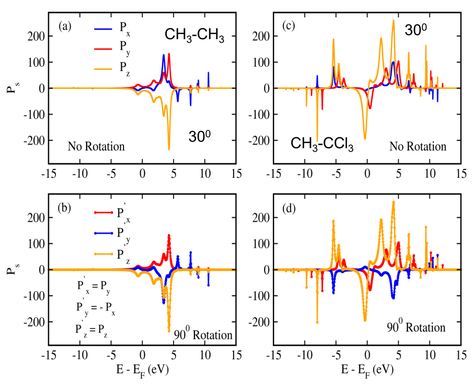
DOS and T (E) for the CH_3-CCl_3 junction

Energy-resolved longitudinal P_z(E)



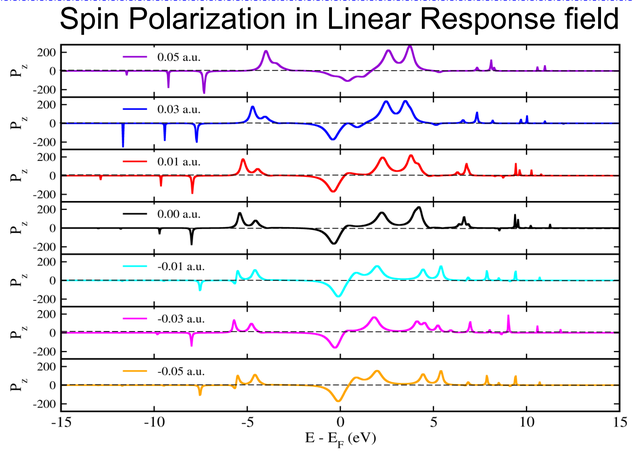
Energy-resolved Ps(E) vector components

Sanity Check



Energy-resolved P_s(E) vector components

Spin Polarization in Linear Response field



P_z(E) component for chiral 30^0 of CH_3-CCl_3 with H leads

Take home message and future goals

- ❖ Electronic chirality is an intrinsic relativistic property of geometrically chiral systems.
- ❖ Dirac relativistic dynamics naturally produces spin-momentum locking without *ad hoc* SOC enhancement, though the calculated spin polarization is far lower than experimental value.
- ❖ Spin-selective transport reflects orbital chirality at the microscopic level.
- ❖ Electric fields control electronic chirality, opening pathways toward tunable chiral spintronics.
- ❖ A next-generation theoretical framework including spin-current-dependent functionals and non-equilibrium effects, is required for quantitative agreement with experiments.

Acknowledgements

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Key References

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Computing resources