Block ☆

The curvature vector $V_m^{(c)}$

The spin-orbit coupling from $i\lambda V_m \cdot \sigma$ has a direct derivation from LL3 §72.

Landau states that the spin-orbit interaction operator for an electron in a self-consistent field as eq (72.7)

$$\hat{V}_{sl} = \sum_a \alpha_a \hat{\mathbf{r}}_a \cdot \hat{\mathbf{s}}_a$$

where $\alpha_a = \hbar^2 / 2m^2 c^2 r \, dU/dr$ is determined by the gradient of the potential $U(r)$. In atomic physics this gives the familiar L·S coupling. For a molecular electron confined to a curved path, the same physics ~~apply~~ applies but the relevant "orbital angular momentum" is not around a nucleus, it is the angular momentum associated with the curved trajectory itself.

When an electron hops between next-nearest sites m and $m+2s$ along a curved chain, it traverses two successive bonds: from m to $m+s$ (unit vector $\hat{d}_{m,s}$) and from $m+s$ to $m+2s$ (unit vector $\hat{d}_{m+s,s}$).

The confinement potential of the molecular chain provides an electric field roughly perp to each bond. The relativistic spin-orbit interaction from LL3 §72 generates an effective magnetic field in ...

... the electron's rest frame proportional to $\bar{E} \times \bar{v}$, where $\bar{v}$ is the electron velocity along the bond.

The cross product of the two successive bond directions:

$\mathbf{v}_m^{(\sigma)} = \hat{d}_{m,s} \times \hat{d}_{m+s,s}$ is exactly the discrete curvature of the chain at site m. It measures how much the chain bends between three consecutive sites. This is precisely the vector that appears in the effective magnetic field $\bar{B} \propto \bar{v}$ when the electron traverses that bend. The spin-orbit coupling from LL3 §72 becomes in the tight binding discretization:

$i\lambda \mathbf{v}_m^{(\sigma)} \cdot \boldsymbol{\sigma}$ where $\boldsymbol{\sigma}$ acts as the spin operator and $\mathbf{v}_m^{(\sigma)}$ plays the role of the effective field direction from §72's eq. (72.3). The factor i comes from the Hermitian structure of the hopping and the convention for the off-diagonal coupling.

Three cases are visible:

Linear chain: all bonds parallel, so $\hat{d}_{m,s} \times \hat{d}_{m+s,s} = 0$. No bending, no effective field. $\mathbf{v}_m^{(\sigma)} = 0$ everywhere, spin-orbit term vanishes completely.

Zig-zag chain: the chain bends within a single plane. The cross product gives $\nu_m^{(3)} = (d_x, d_y, 0)$; a vector lying in that plane, perp to the z-axis. Spin-orbit coupling exists but it is purely transverse; it cannot generate a spin-polarization along the z-axis (transport direction).

Helical chain: The chain twists through 3D-space. Now the cross product acquires a component along the helix axis, giving $\nu_m^{(3)} = (d_x, d_y, d_z)$. The z-component, the longitudinal curvature is crucial! It is the component of spin-orbit coupling that can generate spin polarization along the transport direction, which is what CISS is.

There is also an important asymmetry: $\nu_{m+2s}^{(\tilde{s})} = -\nu_m^{(s)}$ where $\tilde{s} = -s$. Traversing the chain backwards gives the opposite curvature direction. From §13 § 58's rotation picture, this means that the spin rotation acquired going left is the inverse of the rotation going right, a direct mathematical signature of chirality.