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#### Letter

# Spin Fano Resonances in Chiral Molecules: An Alternative Mechanism for the CISS Effect and Experimental Implications

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the coupling strength between the molecule and the lead. Our findings provide another mechanism to explain the experimental observations and lead to new insights into the role of the CISS effect in complex molecules from the perspective of transport and spin polarization resonance, paving the way for chiral moleculebased spintronics applications.

Energy (eV)

**KEYWORDS:** Chiral-induced spin selectivity, spin transport in molecules, spin polarization, spin Fano resonance, near-degeneracy states, Green's function method

#### INTRODUCTION

When electrons pass through a complex chiral molecule, the phenomenon of chiral-induced spin selectivity (CISS) can arise,<sup>1</sup> where the electrons acquire a certain degree of spin polarization due to a combination of space inversion symmetry breaking, induced by the intrinsic chirality of the molecule itself, time-reversal symmetry breaking, and spin-orbit interaction. The phenomenon opens the door to manipulating the spin degree of freedom of electrons in complex quantum biological systems. CISS has attracted growing attention, both experimentally $^{2-10}$  and theoretically. $^{11-24}$  Despite important theoretical research advances in understanding the mechanism for the CISS effect,<sup>22,24</sup> there still remains significant work to do to explain some of the experimental results. In particular, CISS has been observed in various molecular systems such as DNA,<sup>2–4</sup> proteins (bacteriorhodopsin),<sup>5,6</sup> oligopeptides,<sup>7,8</sup> and helicenes.<sup>9,10</sup> The existing experiments can be categorized into four main classes:<sup>25</sup> photoemission,<sup>1,3,5,7,9,26-28</sup> where a laser is shown at a substrate to excite the electrons to go through a chiral molecule, photoexcitation,  $^{29-33}$  in which a low-energy laser in the range of visible light excites an electron-hole pair in a nanoparticle or dye attached to a chiral molecule, transport, <sup>2,6,8,10,34–39</sup> where the chiral molecule is sandwiched between two leads with one lead being ferromagnetic or without a magnetic lead, and electrochemistry,<sup>4,40-42</sup> in which

We also find that the Fano resonance width increases linearly with

the electron conductance through chiral molecules is measured in an electrochemical fluidic cell. Experimentally, the spin polarization associated with current flowing through a chiral molecule as high as 85% has been achieved at room temperatures,<sup>43</sup> and the spin polarization can transport over many tens of nanometers, e.g., through 50 nm chiral perovskite films.<sup>44,45</sup> The purpose of this Letter is to develop a theoretical model for another unexplored mechanism, involving spin Fano resonances, to explain the significant spin polarization associated with CISS.

Twisting angle  $\theta$ 

As a quantum phenomenon at the scale of large biological molecules, CISS is remarkable because the underlying complex molecular system does not possess any intrinsic magnetization that would otherwise affect the spin-dependent responses. Because of the lack of any internal magnetism, a theoretical description of CISS must include spin–orbit coupling (SOC):<sup>46</sup> a weak relativistic effect on the order of a few millielectronvolts. Consequently, in order to achieve appreci-

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able spin polarization, some cumulative effect is necessary, such as multiple scattering<sup>16</sup> in a complex molecule. Specifically, during transport through a large molecule, an electron will encounter, visit, and pass through many atoms. At each encounter where the electron orbits the nucleus, the spin—orbit interaction depends on the orbital orientation, which leads to weak spin polarization. For a large chiral molecule such as DNA, there is a preference in the orbital orientation so the effects on the spin polarization from the many atoms on the electron's way through are cumulatively enhanced, leading to CISS. To understand the experimentally observed large spin polarization has remained a theoretical challenge.

There were previous studies indicating that multiple energy levels can enhance SOC. For example, for coupled nuclear-spin dynamics near a conical intersection, a massive Berry force can arise as the result of even a small amount of SOC, which can in turn dramatically change the pathway selection and result in nearly perfect spin selectivity<sup>47</sup> (close to 100%). Spindependent electron-phonon coupling originated from SOC can introduce an exchange splitting between the spin channels in the structure.<sup>48</sup> The electron correlations originated from molecular vibrations can also lead to the emergence of finite spin polarization in chiral molecules coupled to a metal,<sup>49</sup> where the emergence of a spatially localized polaron due to the electron's coupling with the surrounding lattice distortions can significantly enhance the spin polarization<sup>50</sup> (to about 70%). A theorem based on the Onsager reciprocal principle states that the CISS effect should vanish when thermally averaging over all electron states. However, if the incoming electrons are generated optically, as in experiments, this null result will not arise because of the nonthermal character of the electrons.<sup>23</sup> In a molecular circuit, the molecules represent open systems in contact with electrodes, a fact that tends to be overlooked. The interface between a molecule and a contact surface, particularly a ferromagnetic contact, can provide SOC and can thus be included in the model to explain the large CISS effect.<sup>51,52</sup> In our study, there is no SOC or any related effect from the leads because our focus is on the accumulation effect of SOC inside the molecule.

In electronic transport through mesoscopic, solid-state systems, various resonances in experimental quantities such as conductance and scattering cross sections can arise and are described by the universal Fano formula.<sup>53,54</sup> In terms of spin transport, resonances in the spin polarization arising from the edge of a zigzag graphene nanoribbon were studied using the nonequilibrium Green's function formalism within the framework of density functional theory.<sup>55</sup> Quite recently, a Fano formula characterizing the resonances associated with spin transport was derived.<sup>56</sup> In quantum biology, there were studies of Fano resonances in molecular charge transport.<sup>57,58</sup> For example, control of electronic transport through Fano resonances in molecular wires was investigated using a firstprinciple approach, where the resonances are induced and can be controlled by the side groups attached to the molecule.<sup>59</sup> A similar approach has also been invoked to understand some features of surface enhanced Raman scattering in nonplasmonic nanoparticles.<sup>60</sup> Control of quantum interference in T-shaped molecules was investigated theoretically,<sup>61</sup> and it was found that a Fano resonance can lead to a giant thermal power.<sup>62</sup> Fano resonances can also arise from Andreev reflection in molecular wires.<sup>63</sup> Recent experiments have

exploited conformal control of quantum interference to modulate single-molecule charge transport.<sup>64</sup>

In this Letter, we investigate spin transport through a chiral polyacetylene molecule. Calculating the spin polarization versus the energy, we find the occurrence of a large number of sharp resonances that are characteristic of generalized Fano resonances. To establish this, we derive the Fano formula and test its suitability to describe the numerically observed resonance profiles. In the conventional Fano formula, typically a resonance occurs at a single energy level. However, the structural complexity of the chiral molecule stipulates that level degeneracy is common where, for instance, two energy levels can be arbitrarily close to each other. Our computations reveal that the quasidegeneracy can lead to large spin polarization manifested as a resonance. We find that, in order to explain the resonant enhancement in the spin polarization, both levels must be taken into account, and this leads to a generalized Fano formula. Imposing proper approximations enables us to calculate the resonance width. Based on the energy level spacing and the resonance width, we obtain a criterion to determine whether one or two energy levels are necessary to account for an observed resonance. To our knowledge, prior to our work, spin Fano resonance associated with spin transport in chiral molecules had not been studied. Our finding of Fano resonance-induced and -enhanced spin polarization provides a mechanism to explain some of the experimental results in this field and leads to new insights into understanding and exploiting CISS in transport through complex molecules in general.

#### MODEL AND METHOD

We consider a carbohydrate molecule, namely polyacetylene, a flat chain of conjugated carbon atoms that form a helix with a fixed radius, where each atom is oriented an angle  $\theta$  apart.<sup>23</sup> The pitch of the helix is held fixed so that the geometrical structure of the chain is described by a single parameter: the angle  $\theta$ . An extra hydrogen atom is attached to the carbon atom at both ends. In the limit  $\theta \rightarrow \pi$ , the resulting molecule becomes nonchiral. Each end of the chain is connected to a gold electrode. The starting point is electrons prepared in a localized state in the left lead. A current flows through the molecule while the electrons either pass through the whole molecule to the right lead or are back scattered into the left. A schematic figure of the twisted polyacetylene molecule is shown in Figure 1a.

We employ the standard tight-binding model for the chiral molecule with the generic set of Slater–Koster hopping parameters.<sup>23</sup> For simplicity, we assume that each lead connects only to the outermost carbon atom in the chain. The carbon atoms are modeled using the four n = 2 orbitals, 2s,  $2p_{xy}$   $2p_{yy}$  and  $2p_{zy}$  such that the spinless couplings  $\Gamma$  are positive, semidefinite  $4 \times 4$  matrices. We set the coupling to be diagonal to stipulate that chirality is originated from the molecule, not from the chiral coupling to the lead. In addition, to ensure that the SOC is small in comparison with the coupling to the leads, the diagonal components are set to be  $10\lambda$  to  $100\lambda$ , i.e., ten to hundred times the atomic SOC of a carbon atom, where the coupling constant  $\lambda = 6$  meV.

The general Hamiltonian for the complex molecule can be written as a sum of three terms:

$$\hat{H} = \hat{H}_o + \hat{H}_{SO} + \Sigma \tag{1}$$

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**Figure 1.** Chiral molecule and CISS effect. (a) Illustration of a twisted polyacetylene molecule with filled and open circles denoting carbon and hydrogen atoms, respectively. (b) Spin polarization with respect to energy for a nonchiral ( $\theta = \pi$ ), a left-handedness ( $\theta = \pi/2$ ), and a right-handedness ( $\theta = -\pi/2$ ) molecule, respectively. The number of carbon atoms is N = 8.

where  $\hat{H}_o$  is the molecular spinless Hamiltonian,  $\hat{H}_{SO}$  is the Hamiltonian for spin–orbit coupling (SOC), and  $\Sigma$  is the lead-induced self-energy term. Explicitly, the SOC Hamiltonian can be written as

$$\hat{H}_{SO} = \lambda \boldsymbol{L} \cdot \boldsymbol{\sigma} / \hbar$$

where L is the orbital angular momentum vector and  $\boldsymbol{\sigma} = (\sigma_{x^{j}}, \sigma_{y}, \sigma_{z})$  is the vector of Pauli matrices. The Hamiltonian H preserves the time-reversal symmetry, and there is Kramers degeneracy between the 2-fold degenerate state  $|n\rangle$  and its time-reversed state  $\hat{T}|n\rangle$ .

We use the Landauer formula to calculate the charge and spin current:  $^{\rm 23}$ 

$$T = \mathrm{Tr}\left[\frac{1+\mathbf{a}\cdot\boldsymbol{\sigma}}{2}\gamma_{L}G_{M}^{\dagger}\Gamma_{R}G_{M}\right]$$
(2)

$$S = \operatorname{Tr}\left[\frac{1 + \mathbf{a} \cdot \boldsymbol{\sigma}}{2} \gamma_L G_M^{\dagger} \Gamma_R \boldsymbol{\sigma} \cdot \mathbf{n} G_M\right]$$
(3)

where

$$G_M = \frac{1}{E - H_o - H_{SO} - \Sigma_R - \Sigma_L} \tag{4}$$

is the Green's function for the molecule,  $\Sigma_L$  and  $\Sigma_R$  are the selfenergies from the left and right leads, respectively,  $\Gamma_L$  and  $\Gamma_R$ are the molecular couplings to the left and right leads with  $\Gamma_{L/R} = i[\Sigma_{L/R} - \Sigma_{L/R}^{\dagger}], \gamma_L$  denotes the coupling about how electrons come into the left lead, a is the initial spin direction unit vector, which we set to be zero to assume that there is an equal number of the spin up and down electrons (along the zdirection), and n is the unit directional vector that the spin points at when passing through the molecule. Note that, if all states in the left lead with a given energy are equally probable, which is the case for an equilibrium thermal distribution, then  $\gamma_L$  will be proportional to  $\Gamma_L$ . In this case, combining the Onsager's reciprocal relation with current conservation leads to zero spin polarization. In an actual experiment, the leads are more complicated, where certain initial states in the density matrix are more probable than others so that  $\gamma_L$  is not proportional to  $\Gamma_L$ . A significant CISS effect can then arise. In our study, we inject optically excited electrons to the molecule, thereby breaking the Onsager's reciprocal relation. The spin polarization along a certain direction n is defined as<sup>24</sup>

$$P = \frac{S}{T} \tag{5}$$

We calculate the spin polarization as a function of incident energy E for different values of the twist angle, with a representative example shown in Figure 1b. When there is no chirality, the spin polarization is zero. However, when the molecule is chiral, there are spin polarization peaks, whose



Figure 2. Spin Fano resonance in a chiral molecule. (a) Fano resonance curve for electronic transmission, where the blue solid and black dashed curves are numerical and theoretical results, respectively. (b) Spin Fano resonance curve. The red solid and black dashed curves are numerical and theoretical results, respectively. (c and d) Real and imaginary parts of the total eigenenergies in a certain range, respectively. The number of carbon atoms is N = 8, and the twist angle is  $\theta = \pi/4$ .



Figure 3. Spin Fano resonance in a chiral molecule associated with near-degenerate levels. (a) Fano resonance peak for electronic transmission, where blue solid and black dashed curves are numerical and theoretical results, respectively. (b) Spin polarization Fano resonance peak, with red solid and black dashed curves being numerical and theoretical results, respectively. (c and d) Real and imaginary parts of the eigenenergies, respectively, where the red squares and blue circles represent the exact and perturbation results, respectively. The molecule has N = 27 carbon atoms, and the twist angle is  $\theta = \pi/2$ .

values have opposite signs for the two opposite handednesses. Figure 1b thus illustrates that there are resonant peaks in the spin polarization curve with relatively large spin polarizations.

#### SPIN FANO RESONANCE IN CHIRAL MOLECULES

Utilizing the Green's function method, we have derived the following Fano formula for spin polarization.

$$P = \frac{S}{T} = \alpha \frac{(\epsilon_f + q_f)^2 + y_f}{\epsilon_f^2 + 1}$$
(6)

where the explicit formulas of the different quantities involved are presented in the Supporting Information (SI). The width of the Fano resonance peak  $\gamma_a$  can also be calculated through a perturbation approach (see the SI).

$$\gamma_{\alpha} = -\mathrm{Im}[\langle \psi^{\sigma}_{0\alpha,\mu} | \Sigma | \psi^{\sigma}_{0\alpha,\mu} \rangle] \tag{7}$$

where  $\hat{H}_{c}|\psi_{0\alpha,\mu}\rangle = \epsilon_{0,\alpha}|\psi_{0\alpha,\mu}\rangle$ , with  $\hat{H}_{c} = \hat{H}_{o} + \hat{H}_{SO}$ .

Equation 6 is the Fano resonance formula for spin polarization. To provide numerical validation, we first consider a molecule with eight carbon atoms at the twist angle  $\pi/4$ . Selecting a peak with energy about E = 1.68 eV, we see that the Fano formula (eq 6) matches remarkably well with the numerical curve for both the spin polarization and charge transmission, as shown in Figure 2a and b. From the energy levels in Figure 2c, we have that the two Kramers degenerate states with real part of the energy about 1.68 eV contribute to the spin Fano resonance. The predicted width agrees with the numerical value, as shown in Figure 2d.

#### DEGENERACY ENHANCED SPIN FANO RESONANCE

The Fano resonances presented in Figure 2 result from a single energy level (including the Kramers' degeneracy of two identical levels). For a complex molecule, situations can arise where several nearby energy levels collectively contribute to a resonance. This typically occurs for different twist angles when the number of carbon atoms in the molecule is relatively large. To treat such a case, we include more related Green's function terms in the transmission coefficient in the decomposition of the Green's function (eq S1.12 in the SI). The modified form can be written as

$$G_{\sigma\sigma'}^{R} = G_{\sigma\sigma'}^{0} + G_{\sigma\sigma'}^{1}$$

$$= \sum_{\mu=1,2} \sum_{\beta \neq \alpha} \frac{\psi_{\beta,\mu}^{\sigma}(x_{r}) \Phi_{\beta,\mu}^{\sigma'\dagger}(x_{l})}{E - \epsilon_{\beta}}$$

$$+ \sum_{\alpha} \sum_{\mu=1,2} \frac{\psi_{\alpha,\mu}^{\sigma}(x_{r}) \Phi_{\alpha,\mu}^{\sigma'\dagger}(x_{l})}{E - \epsilon_{\alpha}}$$
(8)

where the second term contains two near-degenerate energy levels contributing to the transmission coefficient. For the spin transmission, we have

$$2S = [(\epsilon_{2}^{2} + 1)\left(\epsilon_{1} + 2q_{1}\frac{\Delta T_{1}}{T^{00}}\right)^{2} + (\epsilon_{1}^{2} + 1) \\ \left(\epsilon_{2} + 2q_{2}\frac{\Delta T_{2}}{T^{00}}\right)^{2} + (\epsilon_{2}^{2} + 1)p_{1} + (\epsilon_{1}^{2} + 1)p_{2} \\ + \epsilon_{1}\epsilon_{2}\frac{4T_{r}^{12}}{T^{00}} - (\epsilon_{1} - \epsilon_{2})\frac{4T_{i}^{12}}{T^{00}} + \frac{4T_{r}^{12}}{T^{00}}]T^{00} \\ /[2(\epsilon_{1}^{2} + 1)(\epsilon_{2}^{2} + 1)]$$
(9)

The details of the derivation and the meaning of each term can be found in the Supporting Information. An exemplary Fano resonance peak with two contributing levels is shown in Figure 3a and b for transmission and spin polarization, respectively. It 2.6 (a)

2.5

2.3 -1.6

2.6

(d)

1.7

1.8

θ

[eV]

ш

1.8

θ

1.9

2.6 (b)

0.8

0.6 2.5

0.4

0.2

0.8

0.6 \_2.5 [eV]

0.4 ш

1.9

ш

2.4

2.3 1.6

2.6

24

(e)

1.7

1.7

1.8

θ

1.9

0.1

0

-0.1

2.3 1.6

2.6

0.05

-0.05

0

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versus the electron energy E and the twist angle  $\theta$  for coupling strength equals to 1 eV. (d-f) Similar plots as those in parts a-c but for a coupling strength of 0.1 eV. The number of carbon atoms is N = 28.

can be seen that the result from the fast-slow variable approximation fits well with the numerical calculation. In a general sense, this is still a Fano resonance, as the corresponding transmission and spin polarization curves can still be fit by a kind of Fano formula.

A challenging question is, given a resonance, how can one determine if it is contributed by a single energy level or by several. Here we provide a criterion to identify the pertinent states by comparing the resonance peak width  $\gamma$  and the energy level spacing between the levels of the resonance peak and its neighbors. As shown in Figure 3c, there are two levels which are quite near the Fano resonance peak with energies E = 2.506and *E* = 2.516, and the energy difference is  $\Delta E$  = 0.01. We then check the corresponding peak width  $\gamma$ , as shown in Figure 3d. We find that the peak widths for the two levels are  $\gamma\approx 0.02$ and  $\gamma \approx 0.015$ , which are larger than the level spacing, so both levels ought to be taken into account when calculating the resonance peak. This peak-width-based criterion can be checked in the single-level case. For example, Figure 2 shows that the resonance peak corresponds to the energy value E =1.676, while the level difference between this level and its nearby levels is about  $\Delta E \approx 0.3$ . We also have that the peak widths for the three levels are  $\gamma = 0.13$ ,  $\gamma = 0.015$ , and  $\gamma =$ 0.014, respectively. These data indicate that there is no significant spin polarization overlap between the central state and its neighboring states, so the resonance is the result of a single energy level.

In comparison with spin Fano resonances due to a single energy level, what effects do nearly degenerate levels have on the resonance? For example, do multiple levels lead to enhanced spin polarization? To address these questions, we focus on the parameter plane of incident energy E and twist angle  $\theta$  and calculate the spin polarization  $P_z$ , the total electronic transmission, and the spin z component transmission in the plane, for a relatively large molecule of N = 28carbon atoms. The results are shown in Figure 4a-c with coupling strength  $c_L = c_R = 1$  eV. It can be seen that, near a level crossing point, a large spin polarization component can emerge, where its sign remains unchanged near the level crossing points. This should be compared with the case of a

nondegenerate region where there is also larger spin polarization but in opposite directions. We examine the spin polarization about the near-degeneracy point and far from the near-degeneracy point and find that two levels contribute to the resonance curve in the former while only one level is involved in the latter case. Detailed criteria for identifying the contribution to the spin Fano resonance as due to two quasidegenerate levels or a single level can be found in the Supporting Information.

#### **EFFECT OF COUPLING STRENGTH ON RESONANCE WIDTH**

The coupling strength between the molecule and the leads can affect the transport behavior and thus the resonance profile. To study this effect, we set the coupling strength to 0.1 and calculate *T*,  $T_z$ , and  $P_z$  in the parameter plane (*E*,  $\theta$ ), as shown in Figure 4d-f, respectively. Comparing the results in Figure 4a and d, we see that the transmission area with values above 0.6 is much larger along the energy axis for the case of unity molecule-lead coupling strength as compared with the case of a smaller coupling strength. A similar behavior occurs for the spin transmission, where a larger area of high transmission along the energy axis near a level-crossing point or a nondegenerate lower single level arises for the large coupling case, as shown in Figure 4b and e. As spin polarization is the ratio between the spin and total charge transmission, the areas in which large polarization transport arises are similar in both cases, as shown in Figure 4c and f.

#### DISCUSSION

Spin-orbit coupling providing a source of magnetic fields for electrons in an atom is a relativistic effect and is thus weak: on the order of a few millielectronvolts. However, it is still possible to generate a sizable spin polarization through some cumulative effect, such as multiple scattering.<sup>16</sup> For example, for transport through a large molecule, an electron will encounter, visit, and pass through many atoms. At each encounter where the electron orbits the nucleus, the spinorbit interaction depends on the orbital orientation and will lead to some weak spin polarization. For chiral molecules such as DNA, there is a preference in the orbital orientation so the effects on an electron's spin polarization from the many atoms on the electron's way through will be cumulatively enhanced, leading to an unexplored variant of the phenomenon of CISS.<sup>1</sup>

It has been a challenge to explain the experimentally observed significant spin polarization caused by the CISS effect for transport through a large molecule. A recent result<sup>23</sup> was that the CISS effect vanishes when all electron states with the same energy are equally likely-a consequence of the Onsager reciprocal principle. Notwithstanding the apparent generality of this result, the CISS effect is observed under nonequilibrium conditions for open systems. In the situation studied here, three important elements need to be taken into account:<sup>23</sup> the electronic states with the same energy not being equally probable (e.g., electrons generated optically by a laser), the presence of accidental degeneracy in the molecular spectrum which enhances the spin-orbit coupling, or a magnetic lead. More recently, an analysis based on symmetry in electronic transmission was carried out to gain insights into the origin of CISS.<sup>24</sup>

The main contribution of this work is the discovery and analysis of spin Fano resonance associated with transport through a complex molecule, which can serve as a plausible mechanism underlying the CISS effects and can explain the experimental findings of relatively large spin polarization under the conditions considered here. Using chiral polyacetylene molecules of different number of carbon atoms, we find the occurrences of various resonance peaks in the curve of spin polarization versus the electron energy. Extending the recently derived formula of spin Fano resonances for transport through a two-dimensional mesoscopic quantum dot<sup>56</sup> to complex molecules, we obtain a general formula for spin Fano resonances, which can be important to quantum biology. Our formula is more general than previous formulas in electronic transport through solid-state devices, because it includes multiple energy levels. This is particularly relevant and important for complex molecules, where quasidegeneracies in the energy levels are ubiquitous. Our formula fits the numerically observed resonance peaks remarkably well for both the straightforward case of a single energy level and the more challenging cases where multiple energy levels are involved. To our knowledge, for the latter case no existing Fano formulas in the literature are applicable. We also develop a criterion for determining the energy levels involved in a Fano resonance, based on the resonance width relative to the spacing of the neighboring energy levels. In general, a spin Fano resonance due to multiple energy levels can lead to enhanced spin polarization, and this can find potential applications in biological-molecule-based spintronics. It should be noted that, at room temperatures, there are atomic oscillations that can affect coherent transport. To ensure coherence, the length of the molecular chain cannot be too large. As a reference, we note that a double-stranded DNA chain with base pairs of up to 80 was used in the experiments.<sup>3</sup> For larger molecules, e.g., a 50 nm chiral perovskite film, effectively the density of states is a continuum. In this case, our model may not be applicable and further investigation is warranted.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c03770.

Derivation of Fano formula, effect of coupling strength, level separation for different twisting angles, criteria for single energy or quasi-degenerate energy contribution to the Fano resonance, change in the atom number, and length and angle dependence of the spin polarization (PDF)

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#### Notes

The authors declare no competing financial interest.

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## Supporting Information for

### Spin Fano Resonances in Chiral Molecules: An Alternative Mechanism for the CISS Effect and Experimental Implications

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#### I. SPIN FANO RESONANCE IN CHIRAL MOLECULES

Because of the inclusion of the self-energy term  $\Sigma$ , the Hamiltonian is non-Hermitian with complex eigenvalues as well as non-identical left and right eigenstates. The eigenequations for the right and left eigenstates, respectively, are

$$\hat{H}|\psi_{\alpha,\mu}\rangle = \varepsilon_{\alpha}|\psi_{\alpha,\mu}\rangle, \qquad (S1.1)$$

$$\langle \phi_{\alpha,\mu} | \hat{H} = \langle \phi_{\alpha,\mu} | \varepsilon_{\alpha}, \tag{S1.2}$$

where  $\mu = 1, 2$  denotes the two Kramer's degenerate eigenstates. The eigenstates  $|\psi_{\alpha,\mu}\rangle$  and  $|\phi_{\alpha,\mu}\rangle$  constitute a biorthonormal basis set under the normalization

$$|\Phi_{\alpha,\mu}\rangle = |\phi_{\alpha,\mu}\rangle/\langle\psi_{\beta,\nu}|\phi_{\alpha,\mu}\rangle. \tag{S1.3}$$

The biorthonormal conditions are

$$\langle \Phi_{\alpha,\mu} | \Psi_{\beta,\nu} \rangle = \langle \Psi_{\alpha,\mu} | \Phi_{\beta,\nu} \rangle = \delta_{\alpha,\beta} \delta_{\mu,\nu}, \qquad (S1.4)$$

with the completeness relation of the eigenwavefunctions

$$\sum_{\mu} \sum_{\alpha} |\Psi_{\alpha,\mu}\rangle \langle \Phi_{\alpha,\mu}| = \sum_{\mu} \sum_{\alpha} |\Phi_{\alpha,\mu}\rangle \langle \Psi_{\alpha,\mu}| = 1.$$
(S1.5)

Using Eqs. (S1.4) and (S1.5), we have the Green's function for the molecule as

$$G^{R}(r,r') = \langle r | \frac{1}{E - \hat{H}} | r' \rangle = \sum_{\alpha,\mu} \sum_{\beta,\nu} \langle r | \Psi_{\alpha,\mu} \rangle \langle \Phi_{\alpha,\mu} | \frac{1}{E - \hat{H}_{s}} | \Psi_{\beta,\nu} \rangle \langle \Phi_{\beta,\nu} | r' \rangle$$
$$= \sum_{\alpha,\mu} \sum_{\beta,\nu} \Psi_{\alpha,\mu}(r) \frac{1}{E - \varepsilon_{\beta}} \delta_{\alpha,\beta} \delta_{\mu,\nu} \Phi^{\dagger}_{\beta,\nu}(r') = \sum_{\mu} \sum_{\alpha} \frac{\Psi_{\alpha,\mu}(r) \Phi^{\dagger}_{\alpha,\mu}(r')}{E - \varepsilon_{\alpha}}$$
$$= \begin{pmatrix} G^{R}_{\uparrow\uparrow}(r,r') & G^{R}_{\uparrow\downarrow}(r,r') \\ G^{R}_{\downarrow\uparrow}(r,r') & G^{R}_{\downarrow\downarrow}(r,r') \end{pmatrix},$$
(S1.6)

where the eigenfunctions are

$$\Phi_{\alpha,\mu}(r') = \begin{pmatrix} \Phi_{\alpha,\mu}^{\uparrow}(r') \\ \Phi_{\alpha,\mu}^{\downarrow}(r') \end{pmatrix}, \qquad (S1.7)$$

$$\Psi_{\alpha,\mu}(r) = \begin{pmatrix} \Psi_{\alpha,\mu}^{\uparrow}(r) \\ \Psi_{\alpha,\mu}^{\downarrow}(r) \end{pmatrix}.$$
(S1.8)

The spin-resolved Green's function can be written as

$$G^{R}_{\sigma\sigma'}(r,r') = \sum_{\mu=1,2} \sum_{\alpha} \frac{\Psi^{\sigma}_{\alpha,\mu}(r) \Phi^{\sigma'\dagger}_{\alpha,\mu}(r')}{E - \varepsilon_{\alpha}}.$$
(S1.9)

where  $\alpha$  denotes the eigenstates corresponding to different eigen energies of the Hamiltonian defined in Eq. (1) in the main text and  $\mu = 1, 2$  denotes the two Kramer's degenerate eigenstates. We

use the Fisher-Lee relation to connect the S matrix with the Green's function [1-3]. The transmission coefficient is given by

$$t_{\sigma\sigma'} = i\sqrt{c_L c_R} G^R_{\sigma\sigma'},\tag{S1.10}$$

where  $c_L$  and  $c_R$  are coupling energies of the molecule to the left and right leads. For each transmission component, we can write

$$T_{\sigma\sigma'} = \operatorname{Tr}(t_{\sigma\sigma'}t_{\sigma\sigma'}^{\dagger}) \tag{S1.11}$$

Based on Green's function formula in Eq. (S1.9), we separate the fast from the slow variables. Let  $E_0$  be the energy. If  $E_0$  approaches an eigenenergy of the corresponding closed system, a pole will arise in R, so we can separate the sum into two terms: one term slowly varying and the other rapidly changing, where the former acts effectively as the background and the latter varies rapidly in the small energy interval. Explicitly, we have

$$G^{R}_{\sigma\sigma'} = G^{0}_{\sigma\sigma'} + G^{1}_{\sigma\sigma'} = \sum_{\mu=1,2} \sum_{\beta \neq \alpha} \frac{\Psi^{\sigma}_{\beta,\mu}(x_r) \Phi^{\sigma'\dagger}_{\beta,\mu}(x_l)}{E - \varepsilon_{\beta}} + \sum_{\mu=1,2} \frac{\Psi^{\sigma}_{\alpha,\mu}(x_r) \Phi^{\sigma'\dagger}_{\alpha,\mu}(x_l)}{E - \varepsilon_{\alpha}}.$$
 (S1.12)

where  $\varepsilon_{\alpha} = E_{\alpha} - i\gamma_{\alpha}$ . The transmission coefficient can be expanded as

$$t_{\sigma\sigma'} = t_{\sigma\sigma'}^0 + t_{\sigma\sigma'}^1. \tag{S1.13}$$

For each transmission component, we can write

$$T_{\sigma\sigma'} = \operatorname{Tr}(t_{\sigma\sigma'}t_{\sigma\sigma'}^{\dagger}). \tag{S1.14}$$

Imposing the approximation about  $\varepsilon_{\alpha}$ , we get the spin transmission as

$$S = \frac{T_{\uparrow\uparrow} + T_{\uparrow\downarrow} - T_{\downarrow\uparrow} - T_{\downarrow\downarrow}}{2} = \frac{T_s^{00}(E_0)}{2} \frac{(\varepsilon + x_s)^2 + y_s}{\varepsilon^2 + 1}.$$
(S1.15)

Similarly, for electronic transmission T, we have

$$T = \frac{T_{\uparrow\uparrow} + T_{\uparrow\downarrow} + T_{\downarrow\uparrow} + T_{\downarrow\downarrow}}{2} = \frac{T_c^{00}(E_0)}{2} \frac{(\varepsilon + x_c)^2 + y_c}{\varepsilon^2 + 1}.$$
(S1.16)

The spin polarization can be written as

$$P = \frac{S}{T} = \alpha \frac{(\varepsilon_f + q_f)^2 + y_f}{\varepsilon_f^2 + 1},$$
(S1.17)

where the explicit formulas of the different variables involved are presented in the next Section.

The width of the Fano resonance peak  $\gamma_{\alpha}$  can also be calculated through a perturbation approach as

$$\gamma_{\alpha} = -\mathrm{Im} \big[ \langle \Psi^{\sigma}_{0\alpha,\mu} | \Sigma | \Psi^{\sigma}_{0\alpha,\mu} \rangle \big]. \tag{S1.18}$$

where  $\hat{H}_c |\psi_{0\alpha,\mu}\rangle = \varepsilon_{0,\alpha} |\psi_{0\alpha,\mu}\rangle$ , with  $\hat{H}_c = \hat{H}_o + \hat{H}_{SO}$ .

#### II. DERIVATION OF FANO FORMULA FOR A SINGLE LEVEL

We derive the Fano formula for spin polarization. Based on the Green's function formula in the main text, we separate the fast from the slow variables. Let  $E_0$  be the energy. If  $E_0$  approaches an eigenenergy of the corresponding closed system, a pole will arise in R, so we can separate the sum into two terms: one slowly varying and the other rapidly changing, where the former acts effectively as the background and the latter varies rapidly in the small energy interval [see Eq. (S1.12)]. The transmission coefficient is given by

$$t_{\sigma\sigma'} = ic_L c_R G^R_{\sigma\sigma'},\tag{S2.19}$$

where  $c_L$  and  $c_R$  are coupling energies of the molecule to the left and right leads, respectively. The transmission coefficient can be written as

$$t_{\sigma\sigma'} = t_{\sigma\sigma'}^0 + t_{\sigma\sigma'}^1. \tag{S2.20}$$

For each transmission component, we have

$$T_{\sigma\sigma'} = \operatorname{Tr}(t_{\sigma\sigma'}t_{\sigma\sigma'}^{\dagger}) = \operatorname{Tr}[(t_{\sigma\sigma'}^{0} + t_{\sigma\sigma'}^{1})(t_{\sigma\sigma'}^{0\dagger} + t_{\sigma\sigma'}^{1\dagger})]$$
  
=  $\operatorname{Tr}(t_{\sigma\sigma'}^{0}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{0}t_{\sigma\sigma'}^{1\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{1}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{1}t_{\sigma\sigma'}^{1\dagger})$   
=  $T_{\sigma\sigma'}^{00} + T_{\sigma\sigma'}^{01} + T_{\sigma\sigma'}^{10} + T_{\sigma\sigma'}^{11}.$  (S2.21)

We impose the following approximations:

$$T^{00}_{\sigma\sigma'}(E) \approx T^{00}_{\sigma\sigma'}(E_0), \tag{S2.22}$$

$$T^{01}_{\sigma\sigma'}(E) \approx T^{01}_{\sigma\sigma'}(E_0) \frac{E_0 - E_\alpha - i\gamma_\alpha}{E - E_\alpha - i\gamma_\alpha} = T^{01}_{\sigma\sigma'}(E_0) \frac{\varepsilon_0 - i}{\varepsilon - i},$$
(S2.23)

$$T^{10}_{\sigma\sigma'}(E) \approx T^{10}_{\sigma\sigma'}(E_0) \frac{E_0 - E_\alpha + i\gamma_\alpha}{E - E_\alpha + i\gamma_\alpha} = T^{10}_{\sigma\sigma'}(E_0) \frac{\varepsilon_0 + i}{\varepsilon + i},$$
(S2.24)

$$T_{\sigma\sigma'}^{11}(E) \approx T_{\sigma\sigma'}^{11}(E_0) \frac{(E_0 - E_\alpha)^2 + \gamma_\alpha^2}{(E - E_\alpha)^2 + \gamma_\alpha^2} = T_{\sigma\sigma'}^{11}(E_0) \frac{\varepsilon_0^2 + 1}{\varepsilon^2 + 1},$$
(S2.25)

where  $\varepsilon \equiv (E - E_{\alpha})/\gamma_{\alpha}$  and  $\varepsilon_0 \equiv (E_0 - E_{\alpha})/\gamma_{\alpha}$ . For  $E_0 = E_{\alpha}$ , we have  $\varepsilon_0 = 0$ . For the spin transmission *S*, we obtain

$$2S = T_{\uparrow\uparrow} + T_{\uparrow\downarrow} - T_{\downarrow\uparrow} - T_{\downarrow\downarrow}$$
  

$$= [T_{\uparrow\uparrow}^{00} + T_{\uparrow\downarrow}^{00} - T_{\downarrow\uparrow}^{00} - T_{\downarrow\downarrow\uparrow}^{00}] + [T_{\uparrow\uparrow\uparrow}^{01} + T_{\uparrow\downarrow\downarrow}^{01} - T_{\downarrow\downarrow\uparrow}^{01} - T_{\downarrow\downarrow\downarrow}^{01}]\frac{\varepsilon_0 - i}{\varepsilon - i}$$
  

$$+ [T_{\uparrow\uparrow\uparrow}^{10} + T_{\uparrow\downarrow\downarrow}^{10} - T_{\downarrow\downarrow\uparrow}^{10} - T_{\downarrow\downarrow\downarrow}^{10}]\frac{\varepsilon_0 + i}{\varepsilon + i} + [T_{\uparrow\uparrow\uparrow}^{11} + T_{\uparrow\downarrow\downarrow}^{11} - T_{\downarrow\downarrow\uparrow}^{11} - T_{\downarrow\downarrow\downarrow}^{11}]\frac{\varepsilon_0^2 + 1}{\varepsilon^2 + 1}$$
  

$$= T_s^{00}(E) + T_s^{01}(E) + T_s^{10}(E) + T_s^{10}(E_0)\frac{\varepsilon_0 + i}{\varepsilon + i} + T_s^{11}(E)\frac{\varepsilon_0^2 + 1}{\varepsilon^2 + 1}.$$
 (S2.26)

Setting  $\varepsilon_0 = 0$  and denoting

$$\Delta T_s = T_s^{01}(E_0) + T_s^{10}(E_0) + T_s^{11}(E_0), \qquad (S2.27)$$

$$q_s = \frac{i}{2} \frac{T_s^{10}(E_0) - T_s^{01}(E_0)}{\Delta T_s},$$
(S2.28)

we get

$$2S = T_s^{00}(E_0) \frac{(\varepsilon + \frac{q_s \Delta T_s}{T_s^{00}})^2 + (1 + \frac{\Delta T_s}{T_s^{00}} - \frac{q_s^2 \Delta T_s^2}{(T_s^{00})^2})}{\varepsilon^2 + 1} = T_s^{00} \frac{(\varepsilon + x_s)^2 + y_s}{\varepsilon^2 + 1},$$
 (S2.29)

where

$$x_s = \frac{q_s \Delta T_s}{T_s^{00}}$$
 and  $y_s = 1 + \frac{\Delta T_s}{T_s^{00}} - \frac{q_s^2 \Delta T_s^2}{(T_s^{00})^2}$ . (S2.30)

Similarly, for spin transmission T, we have

$$2T = T_{\uparrow\uparrow} + T_{\uparrow\downarrow} + T_{\downarrow\downarrow} + T_{\downarrow\downarrow} + T_{\downarrow\downarrow}$$
  
=  $[T_{\uparrow\uparrow}^{00} + T_{\uparrow\downarrow}^{00} + T_{\downarrow\downarrow\uparrow}^{00} + T_{\downarrow\downarrow\downarrow}^{00}] + [T_{\uparrow\uparrow\uparrow}^{01} + T_{\uparrow\downarrow\downarrow}^{01} + T_{\downarrow\downarrow\uparrow}^{01} + T_{\downarrow\downarrow\downarrow}^{01}] \frac{\varepsilon_0 - i}{\varepsilon - i}$   
+  $[T_{\uparrow\uparrow\uparrow}^{10} + T_{\uparrow\downarrow\downarrow}^{10} + T_{\downarrow\uparrow\uparrow}^{10} + T_{\downarrow\downarrow\downarrow}^{10}] \frac{\varepsilon_0 + i}{\varepsilon + i} + [T_{\uparrow\uparrow\uparrow}^{11} + T_{\uparrow\downarrow\downarrow}^{11} + T_{\downarrow\downarrow\uparrow}^{11} + T_{\downarrow\downarrow\downarrow}^{11}] \frac{\varepsilon_0^2 + 1}{\varepsilon^2 + 1}$   
=  $T_c^{00}(E) + T_c^{01}(E) + T_c^{10}(E) + T_c^{11}(E)$   
=  $T_c^{00}(E_0) + T_c^{01}(E_0) \frac{\varepsilon_0 - i}{\varepsilon - i} + T_c^{10}(E_0) \frac{\varepsilon_0 + i}{\varepsilon + i} + T_c^{11}(E) \frac{\varepsilon_0^2 + 1}{\varepsilon^2 + 1}.$  (S2.31)

Setting  $\varepsilon_0 = 0$  and denoting

$$\Delta T_c = T_c^{01}(E_0) + T_c^{10}(E_0) + T_c^{11}(E_0), \qquad (S2.32)$$

$$q_c = \frac{i}{2} \frac{T_c^{10}(E_0) - T_c^{01}(E_0)}{\Delta T_c},$$
(S2.33)

we get

$$2T = T_c^{00}(E_0) \frac{\left(\epsilon + \frac{q_c \Delta T_c}{T_c^{00}}\right)^2 + \left(1 + \frac{\Delta T_c}{T_c^{00}} - \frac{q_c^2 \Delta T_c^2}{(T_c^{00})^2}\right)}{\epsilon^2 + 1},$$
(S2.34)

where

$$x_c = \frac{q_c \Delta T_c}{T_c^{00}}$$
 and  $y_c = 1 + \frac{\Delta T_c}{T_c^{00}} - \frac{q_c^2 \Delta T_c^2}{(T_c^{00})^2}$ . (S2.35)

The spin polarization can be written as

$$P = \frac{S}{T} = \frac{T_s^{00}}{T_c^{00}} \frac{(\varepsilon + x_s)^2 + y_s}{(\varepsilon + x_c)^2 + y_c} = \frac{T_s^{00}}{T_c^{00}} \frac{(\frac{\varepsilon + x_c}{\sqrt{y_c}} + \frac{x_s - x_c}{\sqrt{y_c}})^2 + \frac{y_s}{y_c}}{(\frac{\varepsilon + x_c}{\sqrt{y_c}})^2 + 1} = \alpha \frac{(\varepsilon_f + q_f)^2 + y_f}{\varepsilon_f^2 + 1},$$

which is Eq. (S1.17), where

$$\alpha = \frac{T_s^{00}}{T_c^{00}}, \ \epsilon_f = \frac{\epsilon + x_c}{\sqrt{y_c}}, \ q_f = \frac{x_s - x_c}{\sqrt{y_c}}, \ \text{and} \ y_f = \frac{y_s}{y_c}.$$
 (S2.36)

The width of the Fano resonance peak can also be calculated through a perturbation approach. In particular, with the eigenfunctions in Eqs. (12) and (13) in the main text, and treating the self-energy  $\Sigma$  as a perturbation, we expand the eigenenergies and the eigenstates as

$$\varepsilon_{\alpha} = \varepsilon_{0,\alpha} - \delta_{\alpha} - i\gamma_{\alpha}, \qquad (S2.37)$$

$$|\psi_{\alpha,\mu}\rangle = |\psi_{0\alpha,\mu}\rangle - |\psi_{r\alpha,\mu}\rangle - i|\psi_{i\alpha,\mu}\rangle.$$
(S2.38)

Substituting Eqs. (S2.37) and (S2.38) into Eq. (6) in the main text, we get

$$(\hat{H}_{c}+\Sigma)(|\psi_{0\alpha,\mu}\rangle-|\psi_{r\alpha,\mu}\rangle-i|\psi_{i\alpha,\mu}\rangle) = (\varepsilon_{0,\alpha}-\delta_{\alpha}-i\gamma_{\alpha})(|\psi_{0\alpha,\mu}\rangle-|\psi_{r\alpha,\mu}\rangle-i|\psi_{i\alpha,\mu}\rangle), \quad (S2.39)$$

where  $\hat{H}_c |\psi_{0\alpha,\mu}\rangle = \varepsilon_{0,\alpha} |\psi_{0\alpha,\mu}\rangle$ , with  $\hat{H}_c = \hat{H}_o + \hat{H}_{SO}$ . Left-multiplying  $\langle \psi_{0\alpha,\mu} |$  and after some approximations, we obtain

$$\delta_{\alpha} + i\gamma_{\alpha} \approx -\langle \psi_{0\alpha,\mu} | \Sigma | \psi_{0\alpha,\mu} \rangle. \tag{S2.40}$$

The resonance width  $\gamma_{\alpha}$  is obtained as in Eq. (S1.18).

# III. DERIVATION OF GENERALIZED FANO FORMULA FOR NEAR-DEGENERATE TWO LEVELS

Based on the Green's function formula in the main text, we separate the fast from the slow variables:

$$G^{R}_{\sigma\sigma'}(E) = G^{0}_{\sigma\sigma'} + G^{1}_{\sigma\sigma'} + G^{2}_{\sigma\sigma'} = \sum_{\mu=1,2} \sum_{\beta \neq \alpha_{1},\alpha_{2}} \frac{\Psi^{\sigma}_{\beta,\mu}(x_{r}) \Phi^{\sigma'\dagger}_{\beta,\mu}(x_{l})}{E - \varepsilon_{\beta}} + \sum_{\mu=1,2} \frac{\Psi^{\sigma}_{\alpha_{1},\mu}(x_{r}) \Phi^{\sigma'\dagger}_{\alpha_{1},\mu}(x_{l})}{E - \varepsilon_{\alpha_{1}}} + \sum_{\mu=1,2} \frac{\Psi^{\sigma}_{\alpha_{2},\mu}(x_{r}) \Phi^{\sigma'\dagger}_{\alpha_{2},\mu}(x_{l})}{E - \varepsilon_{\alpha_{2}}}.$$
 (S3.41)

The transmission coefficient is given by

$$t_{\sigma\sigma'} = ic_L c_R G^R_{\sigma\sigma'}, \tag{S3.42}$$

where  $c_L$  and  $c_R$  are coupling energies of the molecule to the left and right leads, respectively. The transmission coefficient can be written as

$$t_{\sigma\sigma'} = t_{\sigma\sigma'}^0 + t_{\sigma\sigma'}^1 + t_{\sigma\sigma'}^2.$$
(S3.43)

For each transmission component, we have

$$T_{\sigma\sigma'} = \operatorname{Tr}(t_{\sigma\sigma'}t_{\sigma\sigma'}^{\dagger}) = \operatorname{Tr}[(t_{\sigma\sigma'}^{0} + t_{\sigma\sigma'}^{1} + t_{\sigma\sigma'}^{2})(t_{\sigma\sigma'}^{0\dagger} + t_{\sigma\sigma'}^{1\dagger} + t_{\sigma\sigma'}^{2\dagger})]$$
  

$$= \operatorname{Tr}(t_{\sigma\sigma'}^{0}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{0}t_{\sigma\sigma'}^{1\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{0}t_{\sigma\sigma'}^{2\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{1}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{1}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{1}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{1\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{10}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0\dagger}) + \operatorname{Tr}(t_{\sigma\sigma'}^{2}t_{\sigma\sigma'}^{0$$

Denoting  $\varepsilon_{\alpha_1} \equiv E_1 - i\gamma_1$  and  $\varepsilon_{\alpha_2} \equiv E_2 - i\gamma_2$ , letting  $E_{01}$  and  $E_{02}$  be constants near  $E_1$  and  $E_2$ , and further denoting  $\varepsilon_1 \equiv (E - E_1)/\gamma_1$ ,  $\varepsilon_2 \equiv (E - E_2)\gamma_2$ ,  $\varepsilon_{01} \equiv (E_{01} - E_1)/\gamma_1$ , and  $\varepsilon_{02} \equiv (E_{02} - E_2)\gamma_2$ , we get

$$T_{\sigma\sigma'}^{00}(E) \approx T_{\sigma\sigma'}^{00}(E_{01}, E_{02}), \tag{S3.45}$$

$$T^{01}_{\sigma\sigma'}(E) \approx T^{01}_{\sigma\sigma'}(E_{01}, E_{02}) \frac{E_{01} - E_1 - i\gamma_1}{E - E_1 - i\gamma_1} = T^{01}_{\sigma\sigma'}(E_{01}, E_{02}) \frac{\varepsilon_{01} - i}{\varepsilon_1 - i},$$
(S3.46)

$$T^{02}_{\sigma\sigma'}(E) \approx T^{02}_{\sigma\sigma'}(E_{01}, E_{02}) \frac{E_{02} - E_2 - i\gamma_2}{E - E_2 - i\gamma_2} = T^{02}_{\sigma\sigma'}(E_{01}, E_{02}) \frac{\varepsilon_{02} - i}{\varepsilon_2 - i},$$
(S3.47)

$$T^{10}_{\sigma\sigma'}(E) \approx T^{10}_{\sigma\sigma'}(E_{01}, E_{02}) \frac{E_{01} - E_1 + i\gamma_1}{E - E_1 + i\gamma_1} = T^{10}_{\sigma\sigma'}(E_{01}, E_{02}) \frac{\varepsilon_{01} + i}{\varepsilon_1 + i},$$
(S3.48)

$$T_{\sigma\sigma'}^{20}(E) \approx T_{\sigma\sigma'}^{20}(E_{01}, E_{02}) \frac{E_{02} - E_2 + i\gamma_2}{E - E_2 + i\gamma_2} = T_{\sigma\sigma'}^{20}(E_{01}, E_{02}) \frac{\varepsilon_{02} + i}{\varepsilon_2 + i},$$
(S3.49)

$$T_{\sigma\sigma'}^{11}(E) = T_{\sigma\sigma'}^{11}(E_{01}, E_{02}) \frac{(E_{01} - E_1)^2 + \gamma_1^2}{(E - E_1)^2 + \gamma_1^2} = T_{\sigma\sigma'}^{11}(E_{01}, E_{02}) \frac{\varepsilon_{01}^2 + 1}{\varepsilon_1^2 + 1},$$
(S3.50)

$$T_{\sigma\sigma'}^{22}(E) = T_{\sigma\sigma'}^{22}(E_{01}, E_{02}) \frac{(E_{02} - E_2)^2 + \gamma_2^2}{(E - E_2)^2 + \gamma_2^2} = T_{\sigma\sigma'}^{22}(E_{01}, E_{02}) \frac{\varepsilon_{02}^2 + 1}{\varepsilon_2^2 + 1},$$
(S3.51)

$$T_{\sigma\sigma'}^{12}(E) = T_{\sigma\sigma'}^{12}(E_{01}, E_{02}) \frac{(E_{01} - E_1 + \gamma_1)(E_{02} - E_2 - \gamma_2)}{(E - E_1 + \gamma_1)(E - E_2 - \gamma_2)} = T_{\sigma\sigma'}^{12}(E_{01}, E_{02}) \frac{(\varepsilon_{01} + i)(\varepsilon_{02} - i)}{(\varepsilon_1 + i)(\varepsilon_2 - i)},$$
(S3.52)
$$(E_1 - E_1 - \gamma_1)(E_1 - E_2 - \gamma_2) = T_{\sigma\sigma'}^{12}(E_{01}, E_{02}) \frac{(\varepsilon_{01} + i)(\varepsilon_{02} - i)}{(\varepsilon_1 + i)(\varepsilon_2 - i)},$$

$$T_{\sigma\sigma'}^{21}(E) = T_{\sigma\sigma'}^{21}(E_{01}, E_{02}) \frac{(E_{01} - E_1 - \gamma_1)(E_{02} - E_2 + \gamma_2)}{(E - E_1 - \gamma_1)(E - E_2 + \gamma_2)} = T_{\sigma\sigma'}^{12}(E_{01}, E_{02}) \frac{(\epsilon_{01} - i)(\epsilon_{02} + i)}{(\epsilon_1 - i)(\epsilon_2 + i)},$$
(S3.53)

where in the approximation  $T_{\sigma\sigma'}^{mn}(E) \approx T_{\sigma\sigma'}^{mn}(E_{01}, E_{02})$  (m = 0, 1, 2, n = 0, 1, 2), we have used  $E = E_{01} + a_0(E_{02} - E_{01})$  with  $a_0 \in [0, 1]$ . The spin transmission *S* is given by

$$\begin{split} 2S &= T_{\uparrow\uparrow} + T_{\uparrow\downarrow} - T_{\downarrow\downarrow} - T_{\downarrow\downarrow} = [T_{\uparrow\uparrow}^{00} + T_{\uparrow\downarrow}^{00} - T_{\downarrow\uparrow}^{00} - T_{\downarrow\downarrow}^{00}] \\ &+ [T_{\uparrow\uparrow\uparrow}^{01} + T_{\uparrow\downarrow\downarrow}^{01} - T_{\downarrow\uparrow\uparrow}^{01} - T_{\downarrow\downarrow\downarrow}^{01}] \frac{\epsilon_{01} - i}{\epsilon_{1} - i} + [T_{\uparrow\uparrow\uparrow}^{02} + T_{\uparrow\downarrow\downarrow}^{02} - T_{\downarrow\downarrow\uparrow}^{02} - T_{\downarrow\downarrow\downarrow}^{02}] \frac{\epsilon_{02} - i}{\epsilon_{2} - i} \\ &+ [T_{\uparrow\uparrow\uparrow}^{10} + T_{\uparrow\downarrow\downarrow}^{10} - T_{\downarrow\uparrow\uparrow}^{10} - T_{\downarrow\downarrow\downarrow}^{10}] \frac{\epsilon_{01} + i}{\epsilon_{1} + i} + [T_{\uparrow\uparrow\uparrow}^{20} + T_{\uparrow\downarrow\downarrow}^{20} - T_{\downarrow\downarrow\uparrow}^{20} - T_{\downarrow\downarrow\downarrow}^{20}] \frac{\epsilon_{02} + i}{\epsilon_{2} + i} \\ &+ [T_{\uparrow\uparrow\uparrow}^{11} + T_{\uparrow\downarrow\downarrow}^{11} - T_{\downarrow\uparrow\uparrow}^{11} - T_{\downarrow\downarrow\downarrow}^{11}] \frac{\epsilon_{01}^{2} + 1}{\epsilon_{1}^{2} + 1} + [T_{\uparrow\uparrow\uparrow}^{22} + T_{\uparrow\downarrow\downarrow}^{22} - T_{\downarrow\downarrow\uparrow}^{22} - T_{\downarrow\downarrow\downarrow}^{22}] \frac{\epsilon_{02}^{2} + 1}{\epsilon_{2}^{2} + 1} \\ &+ [T_{\uparrow\uparrow\uparrow}^{12} + T_{\uparrow\downarrow\downarrow}^{12} - T_{\downarrow\uparrow\uparrow}^{12} - T_{\downarrow\downarrow\downarrow}^{12}] \frac{(\epsilon_{01} + i)(\epsilon_{02} - i)}{(\epsilon_{1} + i)(\epsilon_{2} - i)} + [T_{\uparrow\uparrow\uparrow}^{21} + T_{\uparrow\downarrow\downarrow}^{21} - T_{\downarrow\downarrow\downarrow}^{21} - T_{\downarrow\downarrow\downarrow}^{21}] \frac{(\epsilon_{01} - i)(\epsilon_{02} + i)}{(\epsilon_{1} - i)(\epsilon_{2} - i)} \\ &= T^{00}(E_{01}, E_{02}) + T^{01}(E_{01}, E_{02}) \frac{\epsilon_{01} - i}{\epsilon_{1} - i} + T^{10}(E_{01}, E_{02}) \frac{\epsilon_{01} + i}{\epsilon_{1}^{2} + 1} + T^{22}(E_{01}, E_{02}) \frac{\epsilon_{02} - i}{\epsilon_{2}^{2} + 1} \\ &+ T^{20}(E_{01}, E_{02}) \frac{\epsilon_{02} + i}{\epsilon_{2} + i} + T^{11}(E_{01}, E_{02}) \frac{\epsilon_{01}^{2} + 1}{\epsilon_{1}^{2} + 1} + T^{22}(E_{01}, E_{02}) \frac{\epsilon_{02}^{2} + 1}{\epsilon_{2}^{2} + 1} \\ &+ T^{12}(E_{01}, E_{02}) \frac{(\epsilon_{01} + i)(\epsilon_{02} - i)}{(\epsilon_{1} + i)(\epsilon_{2} - i)} + T^{21}(E_{01}, E_{02}) \frac{(\epsilon_{01} - i)(\epsilon_{2} + i)}{(\epsilon_{1} - i)(\epsilon_{2} + i)} \end{aligned}$$
(S3.54)

Taking  $E_{01} = E_1$  and  $E_{02} = E_2$ , we have  $\varepsilon_{01} = \varepsilon_{02} = 0$ . After a lengthy calculation, we obtain

$$2S = [(\varepsilon_{1}^{2}+1)(\varepsilon_{2}^{2}+1)T^{00} + (1+2\varepsilon_{1}q_{1})(\varepsilon_{2}^{2}+1)\Delta T_{1} + (1+2\varepsilon_{2}q_{2})(\varepsilon_{1}^{2}+1)\Delta T_{2} + 2(\varepsilon_{1}\varepsilon_{2}+1)T_{r}^{12} - 2(\varepsilon_{1}-\varepsilon_{2})T_{i}^{12}]/[(\varepsilon_{1}^{2}+1)(\varepsilon_{2}^{2}+1)] \\ = [(\varepsilon_{2}^{2}+1)(\varepsilon_{1}+2q_{1}\frac{\Delta T_{1}}{T^{00}})^{2} + (\varepsilon_{1}^{2}+1)(\varepsilon_{2}+2q_{2}\frac{\Delta T_{2}}{T^{00}})^{2} + (\varepsilon_{2}^{2}+1)p_{1} + (\varepsilon_{1}^{2}+1)p_{2} \\ + \varepsilon_{1}\varepsilon_{2}\frac{4T_{r}^{12}}{T^{00}} - (\varepsilon_{1}-\varepsilon_{2})\frac{4T_{i}^{12}}{T^{00}} + \frac{4T_{r}^{12}}{T^{00}}]T^{00}/[2(\varepsilon_{1}^{2}+1)(\varepsilon_{2}^{2}+1)]$$
(S3.55)

where

$$\begin{split} \Delta T_1 &\equiv T^{01} + T^{10} + T^{11}, \ \Delta T_2 \equiv T^{02} + T^{20} + T^{22}, \\ q_1 &\equiv \frac{i(T^{10} - T^{01})}{2\Delta T_1}, \ q_2 \equiv \frac{i(T^{20} - T^{02})}{2\Delta T_2}, \\ p_1 &\equiv 1 + \frac{2\Delta T_1}{T^{00}} - 4q_1^2 \frac{\Delta T_1^2}{(T^{00})^2}, \ p_2 \equiv 1 + \frac{2\Delta T_2}{T^{00}} - 4q_2^2 \frac{\Delta T_2^2}{(T^{00})^2}, \\ T_r^{12} &\equiv \Re(T^{12}) \text{ and } \ T_i^{12} \equiv \Im(T^{12}). \end{split}$$

Similarly, we can follow the same procedure, and obtain the charge transmission T as

$$2T = T_{\uparrow\uparrow} + T_{\uparrow\downarrow} + T_{\downarrow\uparrow} + T_{\downarrow\downarrow}$$

$$= \left[ (\epsilon_{2}^{2} + 1)(\epsilon_{1} + 2\tilde{q}_{1}\frac{\Delta\tilde{T}_{1}}{\tilde{T}^{00}})^{2} + (\epsilon_{1}^{2} + 1)(\epsilon_{2} + 2\tilde{q}_{2}\frac{\Delta\tilde{T}_{2}}{\tilde{T}^{00}})^{2} + (\epsilon_{2}^{2} + 1)\tilde{p}_{1} + (\epsilon_{1}^{2} + 1)\tilde{p}_{2} \right]$$

$$+ \epsilon_{1}\epsilon_{2}\frac{4\tilde{T}_{r}^{12}}{\tilde{T}^{00}} - (\epsilon_{1} - \epsilon_{2})\frac{4\tilde{T}_{i}^{12}}{\tilde{T}^{00}} + \frac{4\tilde{T}_{r}^{12}}{\tilde{T}^{00}} \tilde{T}^{00} / [2(\epsilon_{1}^{2} + 1)(\epsilon_{2}^{2} + 1)]$$

$$(S3.56)$$

$$(S3.57)$$

where

$$\begin{split} &\Delta \tilde{T}_{1} \equiv \tilde{T}^{01} + \tilde{T}^{10} + \tilde{T}^{11}, \\ &\Delta \tilde{T}_{2} \equiv \tilde{T}^{02} + \tilde{T}^{20} + \tilde{T}^{22}, \\ &\tilde{q}_{1} \equiv \frac{i(\tilde{T}^{10} - \tilde{T}^{01})}{2\Delta \tilde{T}_{1}}, \\ &\tilde{q}_{2} \equiv \frac{i(\tilde{T}^{20} - \tilde{T}^{02})}{2\Delta \tilde{T}_{2}}, \\ &\tilde{p}_{1} \equiv 1 + \frac{2\Delta \tilde{T}_{1}}{\tilde{T}^{00}} - 4\tilde{q}_{1}^{2} \frac{\Delta \tilde{T}_{1}^{2}}{(\tilde{T}^{00})^{2}}, \\ &\tilde{p}_{2} \equiv 1 + \frac{2\Delta \tilde{T}_{2}}{\tilde{T}^{00}} - 4\tilde{q}_{2}^{2} \frac{\Delta \tilde{T}_{2}^{2}}{(\tilde{T}^{00})^{2}}, \\ &\tilde{T}_{r}^{12} \equiv \Re(\tilde{T}^{12}), \\ &\tilde{T}_{r}^{11} \equiv \Im(\tilde{T}^{12}), \\ &\tilde{T}_{\sigma\sigma'}^{nn} \equiv \tilde{T}_{\sigma\sigma'}^{nnn}(E_{01}, E_{02}) = [T_{\uparrow\uparrow}^{nn} + T_{\uparrow\downarrow}^{nn} + T_{\downarrow\downarrow}^{nn} + T_{\downarrow\downarrow}^{nn}], \end{split}$$

with m = 0, 1, 2, n = 0, 1, 2.

#### IV. EFFECT OF COUPLING STRENGTH ON RESONANCE WIDTH

To further study the transport, we set the twist angle to be  $\theta = 1.69$ , where the Fano resonance peak value is about E = 2.528. Figure S1 shows the transmission versus energy about this resonance. We find that the resonance peak is much narrower for the total transmission and spin transmission in the weak molecule-lead coupling case [comparing Figs. S1(d,e) with Figs. S1(a,b), respectively]. For the spin polarization, the resonance is also narrower in the weak coupling case [comparing Fig. S1(f) with Fig. S1(c)].



FIG. S1. Effect of molecule-lead coupling strength on electronic and spin transport. (a-c) Transmission (*T*), spin-z transmission (*T<sub>z</sub>*), and spin polarization (*P<sub>z</sub>*) versus electron energy *E* for unity molecule-lead coupling strength. (d-f) The corresponding results for the case of coupling strength 0.1. In both cases, the chain has N = 28 carbon atoms and the twist angle is  $\theta = 1.69$ .

To gain more insights, we calculate the imaginary part of the eigenenergy and the resonance peak width versus the molecule-lead coupling strength, as shown in Fig. S2(a). It can be seen that the resonance width increases linearly with the coupling strength. The spin transmission also increases with the coupling strength, as shown in Fig. S2(b). Due to the distinct increasing behaviors in the electronic and spin transmission, the spin polarization first increase, reaches a maximum, and then decreases with the coupling strength, as shown in Fig. S2(c).

# V. QUASIDEGENERACY AND LEVEL SEPARATION FOR DIFFERENT VALUES OF THE MOLECULAR TWIST ANGLE

To assess the effects of fine-tuning the molecular twist angle on the spin polarization resonance, we choose five slightly different angles:  $\theta = 1.61$ , 1.63, 1.65, 1.67, and 1.69, and calculate the spin polarization associated with quasidegenerate energy levels and well separated single energy



FIG. S2. Fano resonance width and peak values versus the molecule-lead coupling strength. (a) Resonance peak width (blue curve) and the imaginary part of eigenenergies (red lines and open circles) versus the coupling strength. (b) Resonance peak values of  $T_z$  versus the coupling strength. (c) Resonance peak values of  $P_z$  versus the coupling strength. The parameter values are N = 28 and  $\theta = 1.69$ . The real part of eigenenergy at the Fano resonance is about E = 2.528.

levels, as shown in Fig. S3. As the angle increases, there is a change in the contribution to the spin polarization resonance from two-state quasidegeneracy points to well separated single-level points. Take the case  $\theta = 1.63$  [Figs. S3(b1-b5)] as an example. Figure S3(b1) shows the energy levels in a certain range. There is a pair of nearby levels with energy E = 2.53 and E = 2.536, where each level corresponds to two degenerate states due to Kramer's degeneracy. Figure S3(b2) shows that the two quasidegenerate levels correspond to two different imaginary parts of the eigenenergies:  $\gamma \approx 0.017$  and  $\gamma \approx 0.014$ , respectively, which determine the width of the spin Fano resonance peak. Figure S3(b3) shows the theoretical result of the spin resonance peak induced by the E = 2.53states, as represented by the black dashed curve, where the red curve is the exact result. The spin resonance peak corresponding to the E = 2.536 states is shown as the black dashed curve in Fig. S3(b4). It can be seen that all these peaks with contribution from a single energy level cannot match the exact spin resonance peak. Note that the theoretical resonance curve in Fig. S3(b3) is wider than that in Fig. S3(b4) due to the larger  $\gamma$  value in the former case. We then insert both levels in the fast changing part of the NEGF formula to produce the corresponding theoretical spin resonance curve, as shown by the black-dashed curve in Fig. S3(b5). In this case, there is a good fit between the theoretical and numerical resonance curves. For the other four rows (corresponding to the four other values of the twist angle), the legends are the same as those in Figs. S3(b1-b5). In Figs. S3(a1-a5), the two target levels are well separated from each other and the exact spin resonance peak is not so sharp. In fact, the theoretical fit from each level or their combination does not produce any result that matches the resonance peak at E = 2.53. For  $\theta = 1.63$  and  $\theta = 1.65$ , as shown in Figs. S3(b1-b5) and Figs. S3(c1-c5), respectively, where the two levels are quite close to each other. While the theoretical resonance curve from each level does not match with the numerical curve, the combination of the two levels produces a spin resonance curve that agrees well with the numerical one. For  $\theta = 1.67$  and  $\theta = 1.69$ , as shown in Figs. S3(d1-d5) and Figs. S3(e1-e5), respectively, the two levels gradually move away from each other. In both cases, the first level (the lower one) gives the correct resonance curve, while the second level does not contribute significantly to the resonance curve. It can then be concluded that, when there are two nearby levels, they contribute collectively to the spin Fano resonance. However, when the levels



FIG. S3. Single level or two quasidegenerate levels contributing to a Fano resonance. (a1) The energy levels for a chiral molecule of N = 28 carbon atoms with the twist angle  $\theta = 1.63$ . (a2) Imaginary part of system eigenenergies. (a3,a4) Examples of single-level contribution to spin Fano resonance for E = 2.53 [black dashed curve, the lower level in (a1)] and E = 2.536 [black dashed curve, the higher level in (a1)], respectively, where the red curves are numerical results from the exact NEGF calculation. (a5) Two-level contribution to spin Fano resonance [black dashed curve, the two levels labeled in (a1)]. The results in panels (b1-b5), (c1-c5), and (d1-d5) are for twist angles  $\theta = 1.65$ , 1.67, and 1.69, respectively, with the same legends as those in (a1-a5).

are well separated from each other, only one level contributes to the resonance peak.

### VI. CRITERIA FOR IDENTIFYING CONTRIBUTION TO SPIN FANO RESONANCE AS DUE TO A SINGLE LEVEL OR TWO QUASIDEGENERATE LEVELS

The results in Figs. 4 in the main text and S3 indicate that a pair of nearby levels, e.g., in the vicinity of a level crossing point, can lead to a large spin Fano resonance peak, to which both levels contribute. Away from the crossing point, there can also be large resonance peaks but they are contributed to by a single state. Here we give a general criterion for identifying whether a spin Fano resonance is due to one or two levels in terms of the energy level difference and the imaginary part  $\gamma$  of the eigenenergy. In particular, denoting the energy of the main state as  $E_1$  and the corresponding energy imaginary part as  $\gamma_1$ , we find the energy level that is the closest to  $E_1$  and denote it as  $E_2$  with imaginary part of the eigenenergy as  $\gamma_2$ . If the level difference  $|E_1 - E_2|$  is

Angle	$E_1$	$E_2$	$ E_1 - E_2 $	$\gamma_1$	γ2	levels
1.62	2.523	2.537	0.015	0.0156	0.0155	two
1.63	2.53	2.536	0.006	0.0168	0.0142	two
1.64	2.531	2.54	0.009	0.0123	0.0183	two
1.65	2.529	2.546	0.017	0.0096	0.02	two
1.66	2.528	2.553	0.025	0.0074	0.021	two
1.67	2.527	2.558	0.031	0.0055	0.0217	one
1.68	2.527	2.562	0.035	0.0043	0.0218	one
1.69	2.528	2.565	0.037	0.0036	0.0214	one

TABLE S1. Identification of one or two-level contribution to spin Fano resonance. The chiral molecule has N = 28 carbon atoms.



FIG. S4. Near-degeneracy enhanced spin Fano resonance. (a) Colored-coded spin-polarization value in the parameter plane of electron energy and molecular twist angle. (b) Magnification of part of (a) about a specific degeneracy point. The chiral molecule has N = 37 carbon atoms.

smaller than or comparable to the larger value of  $\gamma_1$  and  $\gamma_2$ , we deem the second level a contributor to the Fano resonance and include it in the fast changing part of the NEGF formula. Otherwise, we simply choose one level. An example is shown in Table S1.



FIG. S5. Length and angle dependence of the peak value of spin polarization resonance. (a) Peak resonance value versus the carbon atom number for molecule twist angle  $\theta = \pi/2$ . (b) Peak resonance value versus the twist angle for N = 8.

#### VII. SPIN POLARIZATION FOR A CHIRAL MOLECULE OF N = 37 CARBON ATOMS

To provide further support for our finding of near-degeneracy enhanced spin Fano resonance, we calculate the spin polarization in the parameter plane of electron energy and twist angle for a chiral molecule of N = 37 carbon atoms, as shown in Fig. S4. Near the energy-level crossing points, there is significant spin polarization, so is the case for the well separated single levels. In addition,, the spin polarization has negative values about the quasidegenerate points and is positive about the well separated single levels. These results are consistent with those from a chiral molecule of N = 28 carbon atoms in the main text.

#### VIII. LENGTH AND ANGLE DEPENDENCE OF PEAK SPIN POLARIZATION RESONANCE

To confirm the cumulative effect in CISS due to the electron spin-orbit coupling associated with all the atoms in the molecule, we calculate the spin polarization as a function of the carbon atom number *N*. As shown in Fig. S5(a) for  $\theta = \pi/2$ , the spin polarization increases with *N* and reaches the value about 30%, in spite of fluctuations. Figure S5(b) shows the peak resonance value versus the twist angle  $\theta$  for N = 8. Note that, for  $\theta = \pi$ , the molecule is no longer chiral. In this case, the spin polarization peak value is approximately zero. As the angle decreases from  $\theta = \pi$  to  $\theta = \pi/2$ , the molecule becomes progressively more chiral, and the spin polarization increases accordingly, indicating the role of chirality in generating spin polarization.

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