

Spin-orbit coupling in singly charged π -conjugated polymers

J. Rybicki and M. Wohlgenannt*

Department of Physics and Astronomy and Optical Science and Technology Center, University of Iowa, Iowa City, Iowa 52242-1479, USA

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Understanding spin-orbit coupling in singly charged π -conjugated polymer chains is of basic importance to the study of spin transport in organic semiconductors. We show that the spin-orbit coupling is quenched to first order because the diagonal matrix elements vanish and the energy levels in polymers are orbitally nondegenerate. Even the off-diagonal matrix elements are zero or negligibly small unless a twisted nonplanar polymer chain is considered. For such a twisted chain, we calculate these matrix elements using tight-binding wave functions based on p_z orbitals. We show that the Kramers degeneracy prevents the spin-orbit-induced spin precession. Instead, we propose a phonon-assisted spin-flip process and calculate its rate.

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Organic spintronics is an emerging field that studies the dynamics of spin in organic semiconductors.¹⁻³ Organic materials are a promising route to spintronics because the spin-orbit coupling strength is expected to be weak in organic semiconductors, promising long spin-relaxation times. This expectation is based on the observation that these materials are composed mainly of the light elements carbon and hydrogen and the well-known scaling of the spin-orbit coupling strength with the fourth power of the effective charge. However, the atomic carbon spin-orbit coupling strength equals ≈ 6 meV for p states,⁴ which is actually quite strong since it must be compared to the very small interchain hopping matrix elements in organic thin-film devices (typical mobilities are 10^{-5} cm²/V s or less). Therefore the spin-orbit coupling has been proposed by some as the dominant spin-scattering mechanism in organic spin-valve devices.⁵ Moreover, spin-orbit coupling in excitons appears to be quite strong because relatively large intersystem crossing rates between singlet and triplet states can be observed.⁶

On the other hand, studies of the organic magnetoresistive effect⁷⁻¹⁰ (and references therein) suggest that spin-orbit coupling in organics is weaker than the hyperfine coupling. The hyperfine coupling in organics has a strength about ≈ 1 μ eV, and if spin-orbit coupling were indeed weaker than hyperfine coupling, a significant further reduction in the spin-orbit coupling strength compared to the atomic value must result from the binding structure of π -conjugated molecules. These open questions have prompted us to explore the nature of spin-orbit coupling in singly charged conjugated polymer chains. We note that whereas there exist a few works on spin-orbit coupling as it pertains to intersystem crossing between singlet and triplet excitons (Refs. 11 and 12 and references therein), very little seems to be known about spin-orbit coupling in singly charged polymer chains. As we will show below, the treatment of spin-orbit coupling for excitons and singly charged chains is actually quite distinct from each other and quite different conclusions are reached for the two cases.

Because of the chainlike structure of polymers, we use the expression for a nonspherical potential for the spin-orbit coupling Hamiltonian H_{SO} ,

$$H_{SO} = \frac{1}{2m^2c^2}(\nabla V \times \vec{p})\vec{S}, \quad (1)$$

where m is the carrier mass (we will take it to be equal to the free-electron mass in our numerical calculations below), c is the speed of light, V is the potential energy, and \vec{p} and \vec{S} are the linear momentum and spin operators, respectively. Initially, before inclusion of spin-orbit coupling and in the absence of other magnetic interactions the orbital and spin parts of the wave function of the single excess carrier are independent $|\psi\rangle = |\varphi\rangle|\chi\rangle$ and we therefore obtain for a general matrix element of H_{SO} ,

$$\langle\psi_1|H_{SO}|\psi_2\rangle = \frac{1}{2m^2c^2}\langle\varphi_1|\nabla V \times \vec{p}|\varphi_2\rangle\langle\chi_1|\vec{S}|\chi_2\rangle. \quad (2)$$

The spin matrix element—taken between antiparallel spinors—can be readily evaluated, and we will therefore focus on the orbital part of the matrix element. In excitons, however, such a simple splitting into orbital and spinor parts would not be possible since the exchange interaction is quite strong in organic materials, and the orbital wave function in the triplet state is much more tightly bound than in the singlet state.^{13,14}

First we will show, by repeating a well-known proof that the diagonal elements $\langle\varphi_1|\nabla V \times \vec{p}|\varphi_1\rangle$ must vanish. This is because the operator considered is both Hermitian and purely imaginary, whereas the wave function is (or rather can always be chosen to be) purely real. By the Hermitian property, the diagonal matrix elements are real. However they must also be imaginary because the operator is imaginary. Therefore they must be zero to satisfy the two conditions. Moreover, orbitals in π -conjugated polymers are generally nondegenerate (not considering spin). This is because the symmetry group of polymer chains is typically low, allowing only one-dimensional irreducible representations. Therefore, the spin-orbit coupling matrix elements only connect states of different energies and spin-orbit coupling is quenched to first order, since first-order transitions must conserve energy. The situation is distinctly different in atomic carbon. Whereas the spin-orbit coupling matrix elements between, e.g., p_x orbitals is zero by the same argument as presented

above, the spin-orbit coupling is not quenched since it can occur between, e.g., p_x and p_y orbitals and still conserve energy, since they are degenerate. Next we estimate the energy splitting between the lowest and second lowest orbitals. If the wave function is delocalized over the polymer chain (or rather, one of its conjugation segments), the first-excited state will be separated from the lowest state by at least the quantum confinement energy or if the carrier forms a self-localized polaron, the first-excited state is higher in energy by the polaron binding energy. In both cases, the energy difference should be on the order of 100 meV (Ref. 15) and therefore much larger than the spin-orbit coupling energy. The situation may again be very different in excitons, where higher-lying singlet and triplet exciton states could be near degenerate.

Next we will calculate the off-diagonal matrix elements of the spin-orbit coupling for a singly charged polymer chain. The polymer chain is treated in the independent-particle approximation using an effective π -electron tight-binding model, including the electron-phonon coupling to allow for bond dimerization [the so-called Su-Schrieffer-Heeger (SSH) model¹⁶]. Established values for transpolyacetylene for the model parameters are taken,¹⁶ but we do not include a polaronic effect for simplicity. We note that our results should be, at least qualitatively, valid also for other types of polymers, since these more complicated polymers can be mathematically mapped onto polyacetylene with “renormalized” values for the parameters.¹⁴ The matrix elements for H_{SO} are calculated between wave functions obtained using this tight-binding model based on p_z atomic orbitals. We are interested in the spin-orbit coupling for the single excess electron. Spin-other-orbit interactions are neglected. This is a good approximation since all other electrons occupy completely filled bands, either σ bands or the valence band (also called bonding π band), whereas only the excess electron occupies the conduction band (also called antibonding π^* band). This approximation could not be made if we were treating excitonic intersystem crossing, which necessitates a many-particle approach.

Before we embark on the numerical evaluation of the matrix elements for transpolyacetylene, let us analytically treat the problem of the straight-line “polyacetylene,” i.e., lining up the repeat units along a straight line instead of the zig-zag pattern exhibited by real transpolyacetylene. In this case, it can be shown that the y and z components of $\langle \varphi_1 | \nabla V \times \vec{p} | \varphi_2 \rangle$ are zero (where the x axis lies along the line of repeat units) and Eq. (2) can be written in cylindrical coordinates as

$$\langle \varphi_1 | H_{SO} | \varphi_2 \rangle = \frac{1}{2m^2c^2} \langle \varphi_1 | \frac{1}{r} \frac{dV}{dr} L_x | \varphi_2 \rangle \langle \chi_1 | S_x | \chi_2 \rangle, \quad (3)$$

where L_x is the x component of the orbital angular momentum operator. Using this form and using Bloch functions constructed from p_z orbitals as the wave functions, we find that all these matrix elements are also zero, unless one allows for a twist angle θ between neighboring p_z orbitals (we note that bending the polymer chain into a nonplanar geometry also gives nonzero matrix elements, but we will here focus on the case of twisted chains). In this case, it can

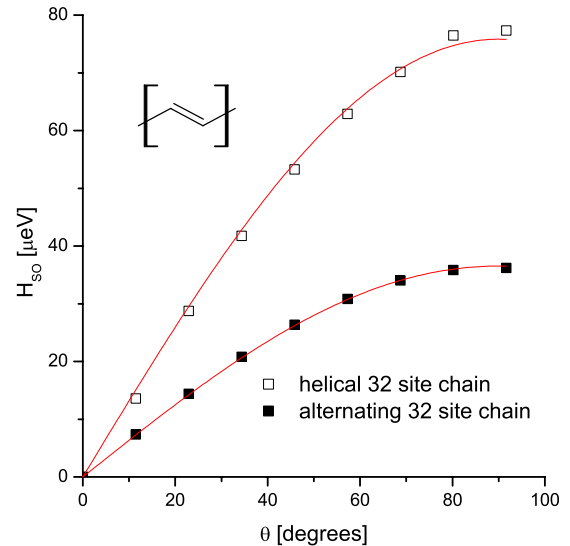


FIG. 1. (Color online) Calculated matrix elements for spin-orbit coupling H_{SO} as a function of the twist angle θ . The matrix element was taken between the orbital ground and first-excited states in a singly charged transpolyacetylene (inset) chain of 32 repeat units. Results are shown both for the case of a helical chain as well as a chain with alternating twist (scatter plots). The solid lines are fits to the law $H_{SO} \propto \sin \theta$.

be shown analytically that $\langle \psi_1 | H_{SO} | \psi_2 \rangle \propto \sin \theta$. In our numerical simulation of the transgeometry, we will also find a dependence similar to $H_{SO} \propto \sin \theta$, although the orbital part of the matrix element will not in general lie completely along the x axis. The conclusion that some sort of twist angle is necessary for the non-negligible spin-orbit coupling in π -conjugated compounds is not restricted to our assumption of using p_z orbitals but follows from symmetry considerations. In the most common symmetry groups for planar polymer structures C_{2h} , C_{2v} , and D_{2h} , the spin-orbit coupling matrix elements are either forbidden or polarized in the out-of-plane direction and therefore negligibly small in planar polymers.¹¹

The SSH model can be solved analytically¹⁶ for the wave function, but we used the numerical diagonalization with Dirichlet boundary conditions. The spin-orbit matrix elements can then be obtained by numerical integration. For the potential, we take a sum of Coulomb potentials with effective charge 4 located at the positions of the carbon atoms in a polyacetylene transchain. We study two cases for the twist angle, namely, helical chains where each p_z orbital is twisted by an additional angle θ compared to the previous atom, starting at $\theta=0$ for the first atom. In a second case, which we will refer to as alternating, the twist angle pattern is assumed to be $0, \theta, 0, \theta, \dots$

Our results for the calculated matrix elements between the orbital ground and first-excited states are shown in Fig. 1 for a 32 site chain. The matrix elements were taken between randomly oriented spinors, and the average over all orientations is plotted in the figures. The data show a dependence approximately proportional to $\sin \theta$ expected from our discussion given earlier. Both results for the helical and alternating chains are similar in magnitude; therefore knowing

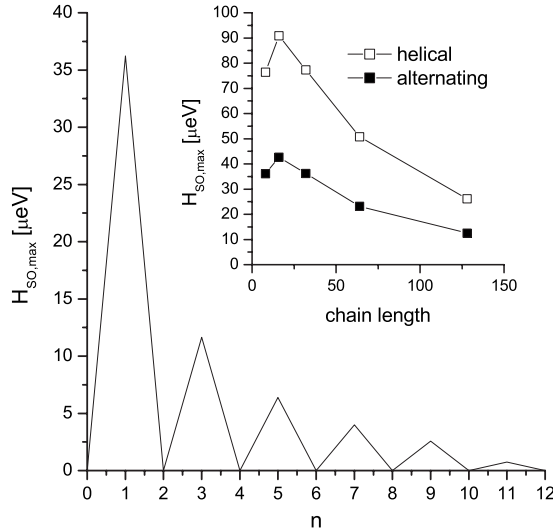


FIG. 2. Calculated values for the maximum ($\theta=90^\circ$) spin-orbit coupling elements $H_{SO,max}$ between the orbital ground and the n th excited states in a singly charged 32 unit chain with alternating twist. Inset: $H_{SO,max}$ as a function of chain length (number of repeat units) both for helical and alternating chains.

the exact twist pattern of a real polymer chain is not crucial. The dependence of the maximum matrix element ($\theta=90^\circ$) as a function of chain length is shown in Fig. 2 (inset). For realistic twist angles of up to $\approx 10^\circ$ (Ref. 17), Fig. 1 shows that we have $H_{SO} \approx 10 \mu\text{eV}$. This is still 1 order of magnitude larger than the hyperfine coupling strength. However, since the diagonal matrix elements are zero, a spin-flip transition cannot occur in first order.

Next we want to treat the second-order effect. For this, we need to calculate the matrix elements between the singly charged ground state, 0, and all excited states n . Figure 2 shows the results for an alternating chain of 32 sites as a function of n . Only the elements between states of opposite parity (odd n) are non-negligible. An analysis shows that the matrix elements decay fast enough with increasing difference in quantum number, so that we can make the following approximation for the effective second-order matrix element H_{SO}^{II} :

$$\langle \uparrow | H_{SO}^{\text{II}} | \downarrow \rangle \equiv \sum_{n,\sigma} \frac{\langle \uparrow | H_{SO} | \sigma \rangle \langle \sigma | H_{SO} | \downarrow \rangle}{E_n - E_0}, \quad (4)$$

$$\approx \sum_{\sigma} \frac{\langle \uparrow | H_{SO} | \sigma \rangle \langle \sigma | H_{SO} | \downarrow \rangle}{E_1 - E_0}, \quad (5)$$

where E_n is the energy of the n th excited state. Since $E_1 - E_0 \approx 100 \text{ meV}$, we expect $H_{SO}^{\text{II}} \approx 1 \text{ neV}$, which is indeed much smaller than the hyperfine coupling.

Next we show that even these higher-order matrix elements do not lead to spin precession. This follows from the time-reversal symmetry, which dictates that in singly charged polymer chains—which have an odd number of electrons—the energy levels must be (at least) doubly degenerate: the so-called Kramers degeneracy. Spin-orbit coupling will indeed mix the pure spin states into pseudospin states, and a

general spin state is a superposition of pseudospin states. Such a superposition, however, will still lie in the degenerate subspace spanned by the pseudospin states and will therefore be conserved.

However, spin-orbit coupling induced spin flips can occur as a phonon-assisted process. The process we have in mind consists of two interactions, once with H_{SO} leading to a spin flip (this interaction does not conserve energy since H_{SO} only couples states with different energies due to orbital nondegeneracy) followed by the absorption of a phonon to enforce the overall energy conservation. To estimate the rate at which this occurs, we derive an expression using the perturbation theory. We write for the matrix element,

$$\langle \uparrow | M | \downarrow \rangle \equiv \sum_n \frac{\langle \uparrow | H_{SO} | \downarrow \rangle \langle H_{\text{ph}} \rangle \left(\frac{2}{qL} \sin \frac{qL}{2} \right)}{E_n - E_0}, \quad (6)$$

$$\approx \frac{\langle \uparrow | H_{SO} | \downarrow \rangle \langle H_{\text{ph}} \rangle \left(\frac{2}{qL} \sin \frac{qL}{2} \right)}{E_1 - E_0}, \quad (7)$$

$$\langle H_{\text{ph}} \rangle \equiv g_\omega \sqrt{n_\omega} \text{ with } \hbar\omega = E_1 - E_0, \quad (8)$$

where g_ω is the matrix element for the absorption of a phonon of frequency ω and wave vector q , and n_ω is the phonon occupation number. The expression within the parentheses results because phonon absorption will not in general obey the momentum conservation at the same time as providing the desired amount of energy. In the following, we will however neglect this term for the purpose of obtaining rough estimates, since we believe that the momentum conservation is relaxed in π -conjugated polymers due to distortions in the polymer chain and polaronic effects which both limit the wave function extent or coherence length L of the excess carrier. The rich phonon spectrum of real polymer chains may also be able to provide phonons with approximately the right energy and momentum at the same time. Next we calculate the rate R from Fermi's golden rule,

$$R = \frac{2\pi H_{SO}^2 |g_\omega|^2 n_\omega}{\hbar (E_1 - E_0)^2} \text{DOS}_{\text{ph}}(E_1 - E_0), \quad (9)$$

$$= \frac{2\pi H_{SO}^2 E_D^2}{\hbar^2 \rho s^3 E_1 - E_0} n_\omega, \quad (10)$$

where, in the second line, we evaluated the phonon matrix element using the deformation potential E_D approach to treating coupling to acoustical phonons. \hbar is Planck's constant, ρ is the linear mass density, s is the speed of sound, and we used the expression for the one-dimensional density of states DOS_{ph} for acoustical phonons. Whereas coupling to acoustical phonons is not the only possibility (optical phonons are known to couple particularly strongly to the carriers in π -conjugated polymers, as evidenced by the “phonon replica” in optical spectra), acoustical phonons have a broad spectrum ideal for providing any desired amount of energy in order for the energy conservation to be fulfilled. We note that, e.g., the scattering of solitons by phonons was previously treated using the deformation-potential approach¹⁸ and that our treatment of the phonon-assisted

spin-flip scattering parallels that given by Miller and Abrahams for phonon-assisted hopping.¹⁹ The most striking property of this phonon-assisted process, irrespective of whether coupling to optical or acoustical phonons is considered, is its activated temperature dependence $n_{\text{ph}} = \exp[-(E_1 - E_0)/kT]$, where k is Boltzmann's constant and T is the temperature. This prediction can be tested in experiments that measure the temperature dependence of the spin-orbit coupling rate.

Although our final expression for acoustical phonons is to some extent phenomenological in π -conjugated polymer chains, we will nevertheless insert values for polyacetylene to obtain a rough estimate for $R: E_D = 3.33$ eV,¹⁸ $v = 1.5 \times 10^4$ m/s,¹⁸ and $\rho = 13u/1.4$ Å, where u is the atomic mass unit. Furthermore we take a typical value for $H_{\text{SO}} = 10$ μeV , as obtained by us above, $E_1 - E_0 = 0.1$ eV. At room temperature, we then obtain $R \approx 10^6$ s⁻¹, which is indeed smaller than the typical hyperfine precession frequency of 1×10^8 to 1×10^9 s⁻¹. Our value for R is in good agreement with a recently obtained experimental value for the spin-lattice relaxation times for a singly charged polyphenylene-vinylene-type polymer $T_{\text{SL}} \approx 30$ μs .²⁰

In summary, we have shown that spin-orbit coupling in singly charged π -conjugated polymer chains is quenched, i.e., no coupling exists in first order. This is because the diagonal spin-orbit coupling elements must vanish, since the

operator is Hermitian and imaginary and because the energy levels in polymers are nondegenerate in the orbital quantum numbers. Indeed, the spacing between the ground and first-excited state is expected to be at least 100 meV. Furthermore, even the off-diagonal matrix elements are zero or negligibly small in planar polymer chains because of symmetry requirements. For twisted nonplanar chains, we calculated the spin-orbit coupling matrix elements between the ground and first-excited states, using tight-binding wave functions based on p_z orbitals, and found values on the order of magnitude of 10 μeV . Moreover, we showed that the matrix elements quickly decay for transitions between more distant eigenstates. Kramers degeneracy prevents spin-orbit induced spin precession, even when taking into account these off-diagonal matrix elements. However, spin-flip transitions can occur as a phonon-assisted process, and we derive an expression for the rate of this process from the perturbation theory. For the acoustic-phonon coupling, we estimate a value for this rate on the order of 1 MHz or less.

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*markus-wohlgenannt@uiowa.edu

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