Nontrivial Bloch oscillation and Zener tunneling frequencies in helicoidal molecules due to spin-orbit coupling

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Bloch oscillation and Zener tunneling are investigated in helicoidal molecules, with DNA as the representative example, in the presence of spin-orbit coupling induced by electrical charges accumulated along the structure of the molecule. We show that the presence of the spin-orbit coupling does not destroy the Bloch oscillations and, further, it induces the appearance of nontrivial Bloch oscillation frequencies associated with resonances among Wannier-Stark states. The Zener tunneling between the spin states is also studied here by looking at the time evolution of the polarization of the wave packet. The results show that the polarization also oscillates with nontrivial well-determined frequencies.

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I. INTRODUCTION

The realization of spintronic devices without the need for the application of an external magnetic field was proposed some years ago in materials with large spin-orbit coupling [1–4]. Although most of the new developments in this area are based on inorganic materials, the efficiency of these devices is still low, requiring cryogenic temperatures or very low intensity output currents [5–7]. Organic molecules have been proposed as candidates to replace inorganic materials in spintronic devices [8–10] because of long spin relaxation time and flexibility. Despite the fact that organic molecules do not present magnetic properties and have low spin-orbit coupling, unconventional spin selectivity has been reported [11–13]. This selectivity originates from the interaction between an inorganic substrate and the organic adsorbed molecule. Recently, however, an unexpected spin selectivity was found in chiral molecules in the absence of any magnetic material [14–17]. From the theoretical point of view, some approaches have been used in order to understand the origin of this spin selectivity. A model based on scattering theory was formulated by Yeganeh et al. to provide a qualitative explanation to the spin selectivity experimentally observed, although it requires unrealistic spin-orbit-coupling values [18]. Gutierrez et al. proposed a minimal model Hamiltonian in order to describe the electron transmission through a helical electrostatic potential. They show that the electric field generated by the charges accumulated along the helix leads to an unconventional Rashba-like spin-orbit (RLSO) interaction [19]. The most recent model proposed shows that beside the RLOS coupling, it is also necessary to take into account the environment-induced dephasing in order to reproduce the experimental results [20,21]. This model also allows us to include the double-chain DNA feature, which is, in this sense, the most realistic model to describe the spin selectivity in DNA molecules.

Here, we focus on the influence of the RLSO coupling on the electronic dynamics in the presence of an external electric field. Indeed, the study of the electronic behavior under the influence of an external electric field is one of the most recurrent issues in condensed-matter physics. To make a long history short, a semiclassical analysis shows that the dynamics of an electronic wave packet placed in an ordered one-dimensional system under the influence of an external electric field displays a completely nontrivial behavior. It follows an oscillatory behavior with characteristic frequency, \(\omega_B = eEA/\hbar\), known as Bloch oscillations (BO) [22]. The experimental observation of electronic BO only was achieved with the ability to grow high-quality semiconductor superlattices [23]. Since this work, the existence of BO has been demonstrated in plenty of systems described by a wave equation. For instance, BO have been reported in ultracold atoms [24,25], Bose-Einstein condensates [26], and light waves in waveguide arrays [27–29]. There are also a great number of theoretical works on this issue, for example, the prediction of BO for one-dimensional long-range correlated disordered systems [30] and in slowly varying aperiodic potentials [31] due to the presence of mobility edges. When electron-electron interaction is considered, a subband of bound electrons is formed, and a frequency doubling of the BO is reported [32]. Furthermore, tunneling between two minibands (Zener tunneling) has been considered recently, bringing up novel features, namely, strong miniband transition for certain values of applied electric field and stable plateaus in the polarization time evolution in the low static field regime [33–35]. It is important to keep in mind that a periodic (or, at least, a correlated nonperiodic) potential is a fundamental requirement for Bloch oscillations: Bloch oscillations can be understood, from the semiclassical point of view, as the electron going in and out of the first Brillouin zone. If disorder takes place, the band structure does not survive, and the Bloch oscillations vanish.

In this work, we show that RLSO coupling presented in [20] does not destroy the BO when an external electric field \(F\) is applied along the molecule (\(z\) direction). Furthermore, we demonstrate the existence of nontrivial frequencies in the BO and in the Zener tunneling (ZT). In order to justify these nontrivial frequencies we provide a semiclassical calculation, and we demonstrate that the new frequencies come from the transitions between Wannier-Stark states with complex energy-level spacing. It is important to stress that, although dephasing processes, such as electron-phonon coupling, are always present, the coherence length is typically bigger...
than the oscillation amplitude [36]. In this sense, dephasing processes, other than the effective disorder caused by the spin-orbit coupling, can safely be disregarded.

II. MODEL

Let us start considering one electron moving in a double-stranded helicoidal molecule subject to an electrostatic potential $V$ due to charges accumulated along the molecule. It was demonstrated that this electrostatic potential leads to a RLSO coupling described, in the second quantization representation, by the Hamiltonian [20,35]

$$H_{SO} = \sum_{j,n} i t_{SO}^j c_{j,n}^\dagger \left[ \sigma_n^j + \sigma_{n+1}^j \right] c_{j,n+1} + \text{H.c.},$$

where $t_{SO}^j = -\alpha^j / 2l_0$ is the spin-orbit-coupling constant, $\alpha = e^2 / m c^2 \nabla V(\mathbf{r})$, and $\sigma_n^j = \sigma_x \sin n \Delta \varphi \sin \theta + \sigma_z \cos n \Delta \varphi \sin \theta + \sigma_2 \cos \theta \cdot l_n$, $\Delta \varphi$, and $\theta$ are, respectively, the arc length, the twist angle between first-neighbor sites, and the helix angle. The total Hamiltonian is given by

$$H = H_{DSM} + H_{SO}.$$  

Here, $H_{DSM} = \sum_{n=1}^N \sum_{j=1}^{N-2} \epsilon_{j,n}^i c_{j,n}^\dagger c_{j,n} + t_{j,n}^i c_{j,n}^\dagger c_{j,n+1} + \lambda_{n} c_{1,n}^\dagger c_{2,n}$ is the usual double-strand Hamiltonian.

It must be stressed here that, although the Hamiltonian of Eq. (2) has been developed for a double-stranded molecule (a double-strand DNA molecule, for instance), it is also valid for single-strand molecules with two levels (the highest occupied and lowest unoccupied molecular orbitals). The solution of the Hamiltonian (2) is a spinor of the form $\psi = (\psi^{(1)}|^\uparrow, \psi^{(1)}|^\downarrow, \psi^{(2)}|^\uparrow, \psi^{(2)}|^\downarrow)^T$, which is similar to the solution of a four-channel tight-binding model, where $\psi^{(j)}|^\sigma$ is the component on the $j$th strand with spin $\sigma$.

In order to observe the BO and the ZT, we perform the time evolution of a wave packet governed by the Schrödinger equation, which is given, in terms of the Wannier amplitudes, by

$$-i\hbar \partial_t \psi_{j,\sigma}^{(1)} = \epsilon_{1(2),j} \psi_{j,\sigma}^{(1)} + V_{1(2)}^{(1)} \psi_{j+1,\sigma}^{(1)} + (V_{1(2)}^{(1)})^* \psi_{j-1,\sigma}^{(1)} + \lambda \psi_{j,\sigma}^{(2)} + W_{1,2}^{(1)} \psi_{j+1}^{(1)} + W_{2,1}^{(1)} \psi_{j-1}^{(1)}$$

$$-i\hbar \partial_t \psi_{j,\sigma}^{(2)} = \epsilon_{1(2),j} \psi_{j,\sigma}^{(2)} + V_{1(2)}^{(2)} \psi_{j+1,\sigma}^{(2)} + (V_{1(2)}^{(2)})^* \psi_{j-1,\sigma}^{(2)} + \lambda^* \psi_{j,\sigma}^{(1)} + (W_{1,2}^{(2)})^* \psi_{j+1}^{(2)} + (W_{2,1}^{(2)})^* \psi_{j-1}^{(2)}$$

where $W_{j,n}^{(1)} = i t_{SO}^j \sin \theta \{ \sin[(n-1)\Delta \varphi] + \sin[n\Delta \varphi] + i \cos[(n-1)\Delta \varphi] + i \cos[n\Delta \varphi] \}$, and preservation of time-reversal symmetry leads to $W_{j,n}^{(2)} = -(W_{j,n}^{(1)})^*$.

The convenient quantities used to characterize the dynamics of the electronic wave packet are the mean position (centroid),

$$x(t) = \sum_{j=1,2} \sum_{n=1}^N (n-n_0) \left| \psi_{j,n}^{(1)} \right|^2 + \left| \psi_{j,n}^{(2)} \right|^2,$$

and the polarization,

$$P(t) = \sum_{j=1,2} \sum_{n=1}^N \left( \left| \psi_{j,n}^{(1)} \right|^2 - \left| \psi_{j,n}^{(2)} \right|^2 \right).$$

\textbf{FIG. 1.} Time evolution of the mean position of an initially Gaussian wave packet for different values of spin-orbit coupling: (a) $t_{SO} = 0.1$, (b) $t_{SO} = 0.2$, and $t_{SO} = 0.3$ meV.
FIG. 2. Fourier transform of the mean position shown in Fig. 1. (a)–(e) Peaks of the Fourier transform of Fig. 1(a). In order to have better visualization, the amplitude of (c) was reduced by a factor of 3250. (f)–(j) Fourier transform peaks of Fig. 1(b) and (k)–(o) peaks of the Fourier transform of Fig. 1(c). Again, in order to have better visualization, (h) and (m) were reduced by a factor of 320 and 80, respectively.

III. RESULTS

Equations (3) and (4) are numerically solved simultaneously by using eighth-order Taylor expansion with a time step $\Delta t \sim 10^{-3}$ time units. Figure 1 shows the time evolution of the mean position $x(t)$ of a Gaussian wave packet with width equal to $l = \Delta z = 0.32$ nm, initially placed at the center of the molecule with up polarization ($\psi_0 = [Ae^{-\left(z-z_0\right)^2/l^2}, 0, 0]^T$), under the influence of an external electric field.

FIG. 3. Time evolution of the spin polarization of an initially polarized Gaussian wave packet for different values of spin-orbit coupling: (a) $t_{SO} = 0.1$ meV, (b) $t_{SO} = 0.2$ meV, and (c) $t_{SO} = 0.3$ meV.
FIG. 4. Fourier transform of the polarization shown in Fig. 3. (a)–(d) Peaks of the Fourier transform of Fig. 3(a). (e)–(h) Peaks of the Fourier transform of Fig. 3(b) and (i)–(l) peaks of the Fourier transform of Fig. 3(c).

$F = 1.5/(\Delta z) \text{meV/nm}$ for three spin-orbit-coupling constant values: $t_{SO}^1 = 0.1 \text{Fig. 1(a)}$, $t_{SO}^1 = 0.2 \text{Fig. 1(b)}$, and $t_{SO}^1 = 0.3 \text{meV Fig. 1(c)}$. Due to the $\pi$ phase of the second chain, we use $t_{SO}^2 = -t_{SO}^1$ [20]. Here we use $\epsilon_{1,j} = -0.3$, $\epsilon_{2,j} = 0.3 \text{meV}$, $\tau = 3 \text{meV}$, and $\lambda = 0.3 \text{meV}$. It must be mentioned that the results reported here are quite robust concerning the choice of the tight-binding parameters. One can see that the electron displays a coherent oscillatory motion over many oscillations with no indication of the oscillation disappearing. There are two noticeable differences between BO in a single band and the present case: The first one is the absence of a characteristic amplitude of the oscillation. The second one is the presence of more than one oscillation frequency.

In order to determine these frequencies, we perform a Fourier transform of the mean position shown in Figs. 1(a), 1(b), and 1(c). The Fourier analyses reveal that peaks are present in five different regions of the spectrum. Moreover, inside each region, the peaks present a nontrivial structure. This behavior is shown in Fig. 2. Figures 2(a), 2(b), 2(c), 2(d), and 2(e) show the peaks of the Fourier transform of the mean position shown in Fig. 1(a). The peak displayed in Fig. 2(c) is nearly where the trivial Bloch frequency would be (e.g., in the absence of spin-orbit coupling), and its amplitude is about 1.325 times bigger than the other peaks (which are all on the same scale). Figures 2(f), 2(g), 2(h), 2(i), and 2(j) exhibit the peaks of the Fourier transform of the mean position shown in Fig. 1(b). One can observe that, in the region where the trivial Bloch frequency was expected, there is a nontrivial structure with six peaks. The amplitudes of these peaks are about 320 times larger than the others shown in Figs. 2(f), 2(g), 2(i), and 2(j) (which also display nontrivial structures). Finally, the peaks of the Fourier transform of Fig. 1(c) are presented in Figs. 2(k), 2(l), 2(m), 2(n), and 2(o). Here, the peaks displayed in Fig. 2(m) are near 80 times bigger than the peaks present in Figs. 2(k), 2(l), 2(n), and 2(o).

It is also interesting to investigate the tunneling between $|\uparrow\rangle$ and $|\downarrow\rangle$ states (ZT). The convenient quantity to look at is the polarization defined by Eq. (6). Figures 3(a)–3(c) show the time evolution of the polarization for three different spin-orbit-coupling constants: $t _{SO}^1 = 0.1 \text{meV}$, $t _{SO}^1 = 0.2 \text{meV}$, and $t _{SO}^1 = 0.3 \text{meV}$. The polarization displays a coherent oscillatory movement over a long time. The frequencies of the oscillation are revealed by the Fourier transform of the polarization, shown in Fig. 4.

Figure 4 reveals that the peaks of the Fourier transform appear in four regions of the spectrum. One can observe that both the mean position and the polarization oscillate with...
the same frequencies, except for the frequencies shown in Figs. 2(b), 2(g), and 2(l), which are not present in the ZT spectrum.

In order to explain the oscillation frequencies and why the frequencies presented in Figs. 2(b), 2(g), and 2(l) are not observed in ZT, we will look at a simplified model of this system. Let us consider the four-channel uniform chain represented in Fig. 5, where each chain represents the spin state of one strand. The magnitudes of the intra- and interchain hopping parameters are also constant throughout the whole system. At first glance, this approach seems to be very unrealistic. However, since the electron is confined in a region that is not very extended, depending on $F$, the parameters observed by the electrons do not have a significant variation.

The Hamiltonian for this system is given by Eq. (2) considering $W_{1,2} = W_{1,2} = W_{2,1}$, $\epsilon_0 = \epsilon_j$ and $\eta = t$. From now on, we shall consider units where $e = 1$ and $\hbar = 1$. Now, consider the velocity operator, given by

$$v = i[H, \mathbf{x}].$$

Using Eq. (7), we can calculate the mean velocity, given by $\text{Tr}(\rho v)$:

The time dependence of expression (8) can be explicitly written in terms of the eigenstates of $H$ (Wannier-Stark states):

$$\tilde{v}(t) = -2\text{Im} \left\{ \sum_{k,k'} \left[ \text{Re}[a_k^* a_k e^{-i(E_k - E_{k'})}] \sum_{j,n} \left( \psi_{k,j,n} \right)^* \left( \psi_{k,j,n+1} \right) + \text{Re}[a_k^* a_k e^{-i(E_k - E_{k'})}] \sum_{j,n} \left( \psi_{k,j,n} \right)^* \left( \psi_{k,j,n+1} \right) \right] \right\},$$

where $E_k$ is the $k$th eigenvalue of $H$ and $\psi_k$ is the eigenvector associated with $E_k$. They must be determined by performing an exact diagonalization of $H$. The coefficients $a_k$ are given by $a_k = \langle \psi_{k,1} | \psi_{k,1} \rangle, \langle \psi_{k,2} | \psi_{k,2} \rangle, \langle \psi_{k,3} | \psi_{k,3} \rangle, \langle \psi_{k,4} | \psi_{k,4} \rangle$.

By integrating Eq. (9) over time, one gets the expression for the mean position of the wave packet:

$$x_{\text{med}}(t) = -2\text{Re} \left\{ \sum_{k,k',k''} \left[ \text{Re}[a_k^* a_k e^{-i(E_k - E_{k'})}] \sum_{j,n} \left( \psi_{k,j,n} \right)^* \left( \psi_{k,j,n+1} \right) + \text{Re}[a_k^* a_k e^{-i(E_k - E_{k'})}] \sum_{j,n} \left( \psi_{k,j,n} \right)^* \left( \psi_{k,j,n+1} \right) \right] \right\},$$

where $E_k$ is the $k$th eigenvalue of $H$ and $\psi_k$ is the eigenvector associated with $E_k$. They must be determined by performing an exact diagonalization of $H$. The coefficients $a_k$ are given by $a_k = \langle \psi_{k,1} | \psi_{k,1} \rangle, \langle \psi_{k,2} | \psi_{k,2} \rangle, \langle \psi_{k,3} | \psi_{k,3} \rangle, \langle \psi_{k,4} | \psi_{k,4} \rangle$.

One semianalytical expression can also be obtained for the polarization; from Eqs. (3) and (4) we can write a master equation for the polarization:

$$\partial_t P(t) = -2\text{Im} \left\{ \sum_{k,k',k''} \left[ \text{Tr}[a_k^* a_k e^{-i(E_k - E_{k'})}] \sum_{j,n} \left( \psi_{k,j,n} \right)^* \left( \psi_{k,j,n+1} \right) + \text{Tr}[a_k^* a_k e^{-i(E_k - E_{k'})}] \sum_{j,n} \left( \psi_{k,j,n} \right)^* \left( \psi_{k,j,n+1} \right) \right] \right\}.$$
important to keep in mind that, due to Kramer degeneracy, each state must be twofold degenerate \[ E(k, \uparrow) = E(-k, \downarrow) \]. The first transition that we analyze is illustrated in Fig. 6, in which the resonance is between a state localized around site \( n \) lying in one strand and another state localized around site \( n \) lying in the other strand. This transition is illustrated in Fig. 6(d). Figures 6(a)–6(c) show the energy difference of the two Wannier-Stark states over \( \hbar \) as a function of the position along the molecule \( n \), with the same SOC parameter used in Figs. 1(a)–1(c) and 3(a)–3(c), respectively.

One can observe that, different from the energy difference of the Wannier-Stark states in the case where SOC is absent, the energy difference is not constant, and it can assume more than one value, leading to the complex peak structure observed in the Figs. 2 and 4. Moreover, each one of the values reported in Figs. 6(a), 6(b), and 6(c) correspond to one peak shown

FIG. 6. Energy difference as a function of the position along the molecule, using (a) \( t_{SO} = 0.1 \) meV, (b) \( t_{SO} = 0.2 \) meV, and (c) \( t_{SO} = 0.3 \) meV. (d) Diagram of the transition in which the energy difference is calculated.

FIG. 7. Energy difference as a function of the position along the molecule, using (a) \( t_{SO} = 0.1 \) meV, (b) \( t_{SO} = 0.2 \) meV, and (c) \( t_{SO} = 0.3 \) meV. (d) Diagram of the transition in which the energy difference is calculated.
in Figs. 2(b), 2(g), and 2(l). It is also interesting to notice that none of these frequencies appear when one is looking at the polarization (Fig. 4). Since the spin-orbit coupling is the only mechanism to flip the spin, transitions involving solely momentum $k$ can change the polarization. Indeed, $k$ does not take place in this transition since it is not a good quantum number in the transverse direction. It can also be verified (not shown here) that if transition that does not involve the wave vector $k$ flipped the spin, the Kramer degeneracy would be removed.

FIG. 8. Energy difference as a function of the position along the molecule, using (a) $t_{SO} = 0.1$ meV, (b) $t_{SO} = 0.2$ meV, and (c) $t_{SO} = 0.3$ meV. (d) Diagram of the transition in which the energy difference is calculated.

FIG. 9. Energy difference as a function of the position along the molecule, using (a) $t_{SO} = 0.1$ meV, (b) $t_{SO} = 0.2$ meV, and (c) $t_{SO} = 0.3$ meV. (d) Diagram of the transition in which the energy difference is calculated.
FIG. 10. Energy difference as a function of the position along the molecule, using (a) $t_{SO} = 0.1$ meV, (b) $t_{SO} = 0.2$ meV, and $t_{SO} = 0.3$ meV. (d) Diagram of the transition in which the energy difference is calculated.

The second transition that we analyze is the one illustrated in Fig. 7(d). It represents a resonance between one Wannier-Stark state lying in one strand, centered at site $n$, and another Wannier-Stark state lying in the other strand, centered on site $n + 1$ (or $n - 1$). Figures 7(a), 7(b), and 7(c) show, respectively, the energy difference (over $\hbar$) as a function of the position along the molecule $n$ for the same SOC parameters used in Figs. 1(a)–(c) and 3(a)–3(c). The frequencies reported here coincide with the frequency peaks shown in Figs. 2(a), 2(f), and 2(k). Observe that these peaks are also present in Figs. 4(a), 4(e), and 4(i), indicating that the transition can happen between a $|\uparrow\rangle$ state and a $|\downarrow\rangle$ state.

Next, we study the transition which leads to the peaks shown in Figs. 2(c), 2(h), and 2(m) and 4(b), 4(f), and 4(j). This transition is represented in Fig. 8(d), and it involves first-neighbor Wannier-Stark states lying in the same strand. Figures 8(a), 8(b), and 8(c) report the frequency due to the transition illustrated in Fig. 8(d) as a function of $n$. One can observe that these frequencies correspond to the oscillation frequencies shown in Figs. 2(a), 2(f), and 2(k) and 4(a), 4(e), and 4(i), respectively.

The structure of peaks presented in Figs. 2(d), 2(i), and 2(n) and 4(c), 4(g), and 4(k) is attributed to the transition shown in Fig. 9(d). Here, the transition is between one state lying in one strand, centered on site $n$, and another state lying in the other strand, localized on site $n + 1$ (or $n - 1$). In Figs. 9(a), 9(b), and 9(c), once more, we show the energy difference between these two states as a function of $n$. Clearly, one can see that they correspond to the frequencies reported in Figs. 2(d), 2(i), and 2(n) and 4(c), 4(g), and 4(k).

Finally, we study in Fig. 10 the last structure of peaks exhibited in Figs. 2(e), 2(j), and 2(o) and 4(d), 4(h), and 4(l). The Wannier-Stark states involved in this transition are lying in the same strand. One of them is localized on site $n$, and the other is localized on site $n + 2$ (or $n - 2$). Indeed, since it involves states that are spatially distant, the overlap of the wave function should not be large, leading to peaks with a very small amplitude, as shown in Figs. 2(e), 2(j), and 2(o) and 4(d), 4(h), and 4(l).

IV. CONCLUSION

In conclusion, we have studied the electronic Bloch oscillations and Zener tunneling in the presence of a helical electric field. It has already been demonstrated that this helicoidal electric field leads to chirality-induced spin-selectivity effects in general chiral molecules [20]. We show that the RLSO coupling induced by the electric field does not destroy the BO and, moreover, it induces the appearance of frequencies that are not present in the absence of the RLSO coupling. The nontrivial frequencies have their origin in the resonance among Wannier-Stark states. In the presence of SOC, the energy difference between two Wannier-Stark states can assume more than one value, leading to a complex structure of Bloch oscillation frequencies. From the experimental point of view, direct observation of such oscillations (either the mean position or the polarization) is still a challenge in organic molecules. Recently, low-temperature scanning tunneling microscopy has been used in order to map the wave function in condensed-matter systems [37], which opens the possibility of experimentally observing many theoretically predicted effects here. An alternative way to achieve the new frequencies could be through a superlattice of accumulated charges along a helicoidal semiconductor.
structure. The ability to grow helicoidal semiconductor structures has already been established [38,39]. Charge excess regions must be deliberately inserted (by inserting a doping material) with specific spacing between them. This procedure generates a helical superlattice of accumulated charges, and the observation of the new frequencies could be possible. We hope that the richness of the phenomena present in the electron dynamics stimulates experimental works in this direction.

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