Bloch Oscillation and Zener Tunneling non-trivial frequencies in helicoidal molecules due to spin-orbit coupling

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

The realization of spintronic devices without the need of the application of an external magnetic field was proposed some years ago in materials with large spin-orbit coupling [1–4]. Although the most of the new development in this area is based on inorganic materials, the efficiency of these devices is still low, requiring cryogenic temperature or with very low intensity output current [5–7]. Organic molecules has been pointed as candidates to replace inorganic materials in spintronic devices[8–10], owing long time spin relaxation time and flexibility. Despite the fact that organic molecules do not present magnetic properties and low spin orbit coupling, unconventional spin selectivity was reported [11–13]. This selectivity is originated by the interaction between the organic subtract and the organic adsorbed molecule. However, recently, an unexpected spin selectivity was found in chiral molecule without any magnetic material [14–17]. From the theoretical point of view, some approaches have been used in order to understand the origin of the spin selectivity. A model based on scattering theory was formulated by Yeganeh et al. providing a qualitative explanation to the spin selectivity experimentally observed, although it needs to use unrealistic spin orbit coupling values [18]. Gutiérrez et al. proposed a minimal model Hamiltonian in order to describe the electron transmission throughout a helical electrostatic potential. The authors 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 necessary to take into account the environment-induced dephasing in order to reproduce the experimental results [20]. This model also allows to include the double chain DNA feature, being, in this sense, the most realistic model in order to describe the spin selectivity in DNA molecules.

Here, we focus on the influence of the RLSO coupling on the electronic dynamics in a presence of an external electric field. Indeed, the study of the electronic behavior under influence of an external electric field is one of the most recurrent issue in condensed matter physics.

To make short a long history: It was shown, by using a semi-classical analyze, that the dynamic of an electronic wave packet placed in an ordered one dimensional system under influence of an external electric field displays a completely non-trivial behavior: It undergoes through an oscillatory movement with a characteristic frequency \( \omega_B = eEa/h \), very known as Bloch oscillations (BO) [21]. The experimental observation of electronic BO only was achieved with the ability of the growing high quality semiconductor super-lattices [22]. Since this work, the existence of BO has been demonstrated in a plenty of systems described by a wave equation. For instance, it has been reported BO in ultacold atoms [23, 24], Bose-Einstein condensates [25] and light waves in waveguides arrays [26–29]. There also is a great number of theoretical works on this issue: It was demonstrated the existence of BO for one dimensional long-range correlated disordered systems [30] and in slowly varying aperiodic potential [31] due to presence of mobility edges. When electron-electron interaction is considered, a sub-band of bound electrons is formed and a frequency doubling of the BO is reported [32]. Tunneling between two mini-bands (Zener Tunneling) has been considered recently bringing up new very interesting features: Strong mini-bands transition occurs for certain values of applied electric field, stables plateaus in the polarization time evolution in the low static field regime [34].

In the present work, we show that RLSO coupling presented in [20] does not destroy the BO, when an external electric field, \( F \), is applied in the \( z \) direction,e.g., along the molecule. Furthermore, we show the existence of nontrivial frequencies in the BO and in the Zener tunneling. In order to justify these nontrivial frequencies we provide a semi-analytical calculation and demonstrated that the new frequencies come from the resonances among opposite spin polarization Wannier-Stark states.

Let us start considering one electron moving in a double strand 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]:

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\[ H_{SO} = \sum_{j,n} i t_{SO}^{l} c_{j,n}^\dagger [\sigma^x_{j,n} + \sigma^y_{j,n+1}] c_{j,n+1} + H.c. \]  

(1)

where \( t_{SO}^{l} = -\alpha^l/2l_c \), \( \alpha = \frac{k^2}{m_e}\frac{dV(x)}{dx} \) and \( \sigma^x_{j,n+1} = \sigma_x \sin n\Delta\phi \sin \theta + \sigma_y \cos n\Delta\phi \sin \theta + \sigma_z \cos \theta. \ l_c, \ \Delta\phi \) and \( \theta \) are, respectively, the arc length, the twist angle between first neighbor sites and the helix angle. The total Hamiltonian is given by:

\[ H = H_{DSM} + H_{SO} \]  

(2)

Here, \( H_{DSM} = \sum_{n=1}^{N} \sum_{j=1}^{2} \varepsilon_{j,n} c_{j,n}^\dagger c_{j,n} + t_{j,n} c_{j,n}^\dagger c_{j,n+1} \) is the usual double strand Hamiltonian.

It must be stressed here that, although the Hamiltonian of the equation 2 has been developed for a double strand molecule (a double strand DNA molecule, for instance), it also is valid for a single strand molecules with two levels (HOMO and LUMO). The solution of the Hamiltonian 2 is a spinor of the form \( \psi = (\psi_1^{(1)}, \psi_1^{(2)}, \psi_2^{(1)}, \psi_2^{(2)})^T \), which similar to the solution of a four channel tight binding model.

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

\[-i \hbar \partial_t \psi_1^{(2)\dagger} = \varepsilon_1^{(2)} \psi_1^{(2)\dagger} + V^{(2)} \psi_{j+1}^{(2)\dagger} + V^{(1)} \psi_1^{(1)\dagger} \]

\[+ \lambda \psi_j^{(1)\dagger} + W_{1,2}^{(1)} \psi_{2,j+1}^{(1)\dagger} + W_{1,2}^{(1)} \psi_{2,j}^{(1)\dagger} \]  

(3)

\[-i \hbar \partial_t \psi_1^{(2)\dagger} = \varepsilon_1^{(2)} \psi_1^{(2)\dagger} + V^{(2)} \psi_{j+1}^{(2)\dagger} + V^{(1)} \psi_1^{(1)\dagger} \]

\[+ \lambda^* \psi_j^{(1)\dagger} + (W_{1,2}^{(1)})^* \psi_{2,j+1}^{(1)\dagger} + (W_{1,2}^{(1)})^* \psi_{2,j}^{(1)\dagger} \]  

(4)

where \( W_{1,2}^{(1)} = \frac{it_{SO} \sin \theta}{\sin[(n-1)\Delta\varphi]} + \frac{i\sin[n\Delta\varphi]}{\sin[(n-1)\Delta\varphi]} \). The preservation time reversal symmetry leads to \( W_{1,2}^{(1)} = -(W_{1,2}^{(1)})* \).

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

\[ x(t) = \sum_{j=1,2} \sum_{n=1}^{\infty} (n - n_0)(|\psi_1^{(2)}|^2 + |\psi_2^{(1)}|^2) \]  

(5)

and the polarization,

\[ P(t) = \sum_{j=1,2} \sum_{n=1}^{\infty} (|\psi_1^{(2)}|^2 - |\psi_2^{(1)}|^2) \]  

(6)

The equations 3 and 4 are numerically solved simultaneously by using 8th order Taylor’s expansion with 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 (\( \psi_0 = [Ae^{-\frac{(x-0.6)^2}{2}}, 0, 0, 0]^T \), under action of an external electric field \( F = 1.5/\Delta z \) meV/nm, for three SOC values: (a) \( t_{SO} = 0.2 \), (b) \( t_{SO} = 0.3 \) and (c) \( t_{SO} = 0.4 \) meV nm and \( t_{SO} = -t_{SO} \) [20]. Here we use \( \varepsilon_{1,j} = -0.3 \), \( \varepsilon_{2,j} = 0.3 \) meV and \( t = 3 \) meV. One can see that the electron displays a coherent oscillatory motion over many oscillations with no indication of the disappearing of the oscillation. 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.

It is also interesting to investigate the tunneling between the |↑⟩ and |↓⟩ states (ZT). The convenient quantity to look at is the ZT is the polarization defined in the equation 6. The figure 2 shows the time evolution of the polarization for three different spin-orbit coupling constant: (a) \( t_{SO} = 0.2 \), (b) \( t_{SO} = 0.3 \) and (c) \( t_{SO} = 0.4 \) meV nm and theirs respective Fourier Transformed, (d), (e) and (f). One can see that, in addition to the trivial frequency \( \omega_B \), there is the appearing of non trivial frequencies.
The eigenvector associated with $\alpha$ of an initially polarized gaussian wave packet for different values of $\alpha$: (a) $\alpha = 0.1$, (b) $\alpha = 0.2$ and (c) $\alpha = 0.3$ meV nm. Right panel: Fourier Transformed of the spin polarization with different values of a) $t_{SO} = 0.2$, (b) $t_{SO} = 0.3$ and $t_{SO} = 0.4$ meV nm

![Figure 2: Left panel: Time evolution of the spin polarization of an initially polarized gaussian wave packet for different values of $\alpha$: (a) $\alpha = 0.1$, (b) $\alpha = 0.2$ and (c) $\alpha = 0.3$ meV nm. Right panel: Fourier Transformed of the spin polarization with different values of a) $t_{SO} = 0.2$, (b) $t_{SO} = 0.3$ and $t_{SO} = 0.4$ meV nm.]

![Figure 3: Representation of the four channel tight binding model (see equations 3 and 4).](image)

Look at a simplified model of this system. Let us consider a four channel uniform chain represented in the figure 3, where each chain represents the spin state of one strand.

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

$$\bar{v}(t) = -23 \left\{ \sum_{k,k'} \left[ \mathcal{R}[t]a_k^* a_{k'} e^{-i(E_{k'} - E_k)t} \sum_{j,n} (\varphi_{k}^{\uparrow})^*_{n} (\varphi_{k'}^{\uparrow})_{n+1} + \mathcal{R}[t]a_k^* a_{k'} e^{-i(E_{k'} - E_k)t} \sum_{j,n} (\varphi_{k}^{\downarrow})^*_{n} (\varphi_{k'}^{\downarrow})_{n+1} \right] + \left[ W_{2,1}^j a_k^* a_{k'} e^{-i(E_{k'} - E_k)t} \sum_{j,n} (\varphi_{k}^{\uparrow})^*_{n} (\varphi_{k'}^{\uparrow})_{n+1} + W_{1,2} a_k^* a_{k'} e^{-i(E_{k'} - E_k)t} \sum_{j,n} (\varphi_{k}^{\downarrow})^*_{n} (\varphi_{k'}^{\downarrow})_{n+1} \right] \right\} \right\}$$

where $E_k$ is the $k^{th}$ eigenvalue of $H$ and $\varphi_k$ 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: $a_k = (\varphi_k^{\uparrow}, \varphi_{k'}^{\uparrow}, \varphi_{k}^{\downarrow}, \varphi_{k'}^{\downarrow})^T$.

Integrating the equation 9 over the time, one gets the expression to the mean position of the wave packet:

$$\mathcal{R}[t]a_k^* a_{k'} e^{-i(E_{k'} - E_k)t} \sum_{j,n} (\varphi_{k}^{\uparrow})^*_{n} (\varphi_{k'}^{\uparrow})_{n+1}$$
\[ x_{\text{med}}(t) = -2\Re \left\{ \sum_{k,k',k \neq k'} \left[ \frac{\mathcal{R}[a_k^* a_{k'}]}{(E_k - E_{k'})} e^{-i(E_k - E_{k'})t} \sum_{j,n} (\varphi_{k'}^j)^* \varphi_{k}^{j+1} \right] + \frac{\mathcal{R}[a_k^* a_{k'}]}{(E_k - E_{k'})} e^{-i(E_k - E_{k'})t} \sum_{j,n} (\varphi_{k'}^j)^* \varphi_{k}^{j+1} \right\} + x_0. \] (10)

One semi-analytical expression also can obtained for the polarization. From the equations 3 and 4 we can write a master equation of the polarization:

\[ \partial_t P(t) = -23 \left\{ \sum_{k,k'} (W_{1,2}^j)^* a_k a_{k'} e^{-i(E_k - E_{k'})t} \sum_{j,n} (\varphi_{k'}^j)^* \varphi_{k}^{j+1} \right\} \] (11)

Integrating the equation 11 over time, one gets the equation for the polarization:

\[ P(t) = 4\Re \left\{ \sum_{k,k',k \neq k'} \left[ -\frac{a_k^* a_{k'}}{(E_k - E_{k'})} e^{i(E_k - E_{k'})t} \sum_{j,n} (\varphi_{k'}^j)^* \varphi_{k}^{j+1} \right] \right\} + P_0 \] (12)

From the equations 10 and 12 it is possible to understand the figures 1 and 2: Either the trivial Blo frequency \( \omega_B \) or the non-trivial frequencies are explained in terms of resonances of Wannier-Stark states as predicted by the above equations. The frequencies are determined by the difference among the Wannier-Stark energy levels. The spectrum consist in four interpenetrating Wannier-Stark ladder: \( E_{2n}^{\phi,t(\pm)} = \epsilon_0 + r_j^{\pm} + m e F \Delta z \) \[ 37 \], where \( r_j^{\pm} \) must be determined numerically and may depend on \( t_B \) and on the external field. In this sense, one expects that Fourier components in \( x_{\text{med}} \) and \( P \) occur at: \( \omega = m e F \Delta z \), which are the trivial Bloch frequencies. The physical origin of these frequencies is the resonance between two Wannier-Stark states with same spin polarization and lied in the same strand. The non-trivial frequencies must appear at: \( \omega = \pm e F \Delta z (r_j^{\sigma} - r_j^{\sigma'}) + m e F \Delta z \), where \( \sigma \) and \( \sigma' \) are the spin polarization. Thus, the non-trivial frequencies appear due to resonance Wannier-Stark states with different polarization or lied in different strand. It must be observed that the slowest frequencies are determined by the minimal distance (in energy) between two Wannier-Stark state and all the other frequencies are specified by them. A qualitative understanding of the frequencies can be provide by using similar arguments to the semi-classical approach. In this approximation, the momentum of the electron is given by: \( \hbar k(t) = \hbar k_0 + e F t \). For a time independent electric field, \( \hbar k(t) = \hbar k_0 + e F t \). One can calculate the electronic velocity using that \( v_n(k) = \partial \epsilon_n(k)/\partial k \). In this case, there are four mini-bands. If the electron accelerates lied in a single mini-band, it cross the first Brillouin zone in \( T_B = 1/\omega_B \). However, the electron can jump from one band to another and, thus, changing the response (or, in semi-classical terms, the acceleration) to the electric field. In this sense, the electron movement depends in which mini band the electron is, leading to new frequencies.

In conclusion, we have studied the electronic Bloch Oscillations and the Zener tunneling in the presence of helical electric field. It already has been demonstrated that
this helicoidal electric field leads to a 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 non trivial frequencies have their origin in the resonance among Wannier-Stark states. From the experimental point of view, the direct observation of such oscillation (either the mean position or the polarization) still is challenger in organic molecules and we hope that the richness of the phenomena present in the electron dynamic stimulates the experimental works in this direction.

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I. REFERENCES