Research of spin-orbit interaction in organic conjugated polymers

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Abstract. The effect of spin-orbit interaction on the one-dimensional organic polymer was investigated theoretically. Spin-orbital interaction led to the spatial separation of energy band but did not eliminate spin degeneration, which was different from energy level splitting in the Zeeman Effect. Spin-orbit interaction had little effect on the energy band structure, charge density, and lattice position, etc.; Spin precession was obtained when a polaron was transported along the polymer chain, which theoretically proved that it was feasible to control the spin precession of polaron in organic polymers by the use of external electric field.

1. Introduction

In 1990, Datta and Das proposed the idea of FET field-effect transistor, which controlled the electron spin precession effectively through the Rashba spin-orbit interaction [1]. Since then, the spin-orbit interaction had become the hot research topic in the semiconductor spin electronics [2-11]. The strength of the effect of Rashba has been realized by using an applied electric field in the experiment. The energy band structure, electronic wave function, spin angular velocity and the linear velocity, electric conductivity of the quasi one-dimensional electron gas system can all be influenced by the Rashba spin-orbit interaction.

At present, the research on organic spin electronics has just started [12-16]. In theory, some new phenomena related to spin are predicted, and the experimental results also confirmed that the spin polarized current could exist in the organic body. In organic semiconductors there are few previous studies on the spin-orbit interaction, because it is generally believed that the spin-orbit interaction in organic semiconductors is slight, but its impact is inevitable. This paper will discuss the change of one-dimensional organic polymers under spin-orbit interaction.

2. Spin-orbit coupling effect on the electronic structure of organic conjugated polymers

The system which we are studying is the one-dimensional organic polymers with non-degenerate ground state. Assuming that one-dimensional organic polymer chain points to the x axis, we add an electric field (Rashba electric field) in the z axis, Rashba electric field is used to regulate the spin-orbit interaction, and the Hamiltonian of spin-orbit coupling effect is expressed as:

\[ H_{SO} = i\gamma \left( \sigma_x \frac{\partial}{\partial y} - \sigma_y \frac{\partial}{\partial x} \right) \]  

(1)
In the equation (1) we only retain the second term in the brackets, because the one-dimensional organic polymer chains points to the x direction. In which \( \gamma = \frac{\hbar^2 E_{SO}}{4m_e^2c^2} \) is a constant representing spin-orbit interaction. \( c, e, m_e \) are the speed of light, the electronic quantity and the electron quality respectively. \( E_{SO} \) describes the quantities of Rashba electric field, and \( \sigma_y \) is the Pauli matrix.

We can get the one-dimensional tight binding model through the second quantization:

\[
H_{SO} = -t_{SO} \sum_n \left[ C_{n+1, \uparrow} C_{n, \downarrow} - C_{n+1, \downarrow} C_{n, \uparrow} + C_{n, \downarrow} C_{n+1, \uparrow} - C_{n+1, \uparrow} C_{n, \downarrow} \right]
\]

(2)

in which \( t_{SO} = \gamma / 2a \), \( t_{SO} \) is the quantities of the Rashba spin-orbit coupling, which describes the transition integral of electrons in adjacent grid points, and \( a \) is the lattice constant. \( C_{n,s} (C_{n,s}) \) is the generation (disappearance) operator of an electron at a lattice point \( n \).

The Hamiltonian of electronic partion includes the polymer that is represented by the extended one-dimensional tight binding model and the spin-orbit coupling portion represented by one-dimensional tight binding model.

\[
H_e = H_{SSH} + H_{so}
\]

(3)

\[
H_{SSH} = -\sum_{n,s} t_0 - \alpha (u_{n+1} - u_n) (-1)^n t_e \sum_{n,s} \left[ C_{n+1,s} C_{n,s} + C_{n,s} C_{n+1,s} \right]
\]

(4)

\[
H_{SO} = -t_{SO} \sum_n \left[ C_{n+1, \uparrow} C_{n, \downarrow} - C_{n+1, \downarrow} C_{n, \uparrow} + C_{n, \downarrow} C_{n+1, \uparrow} - C_{n+1, \uparrow} C_{n, \downarrow} \right]
\]

(5)

in which \( \alpha \) is the electron-phonon coupling constant, \( t_e \) is degenerate parameter, \( t_0 \) is the transition integral of electrons in adjacent grid points \( n \) and \( n+1 \), \( u_n \) is the position deviation of the \( n \) lattice point(CH group).

The electronic energy spectrum can be obtained by Fourier transform:

\[
E(k) = \pm 2t_{SO} \sin(ka) + E_0(k)
\]

(6)

\[
E_0(k) = \left[ (-2t_0 \cos(ka))^2 + (4\alpha u \sin(ka))^2 \right]^{\frac{1}{2}}
\]

(7)

Rashba spin-orbit interaction leads the spatial separation between “\( y^+ \)” (along the \( \tilde{y} \) axis) and “\( -\tilde{y} \)” (along the \( \tilde{y} \) axis) spinor components (One-dimensional organic polymer points to the x direction, and Rashba electric field is along the \( z \) direct). The Zeeman effect can also lead to the spatial separation, but the spatial separation which is induced by Rashba spin-orbit coupling is different from the energy splitting caused by the Zeeman effect, because the spin merger is not eliminated. Spin-orbit interaction induces wider energy band of organic conjugated polymer and narrower energy gap, but the change is not very obvious as a result of the weak spin-orbit coupling in the organic polymer. The lattice configuration and the charge density of the carriers in organic polymer such as polarons and bipolarons, do not change significantly.

3. Spin-orbit coupling effect on the polaron transport in organic polymer
Spin-orbit interaction will produce when the electrons are moving in the influence of asymmetric potential, which is closely connected to the charge motion. The physical image of the transport...
dynamics of organic polymers is needed to be studied so as to understand the effect of spin-orbit coupling deeply. In this paper, we study the effect of spin-orbit interaction on polaron (carrying the single charge and 1/2 spin) transport in one dimensional organic polymer.

The electric field is added in the direction parallel to the one dimensional organic polymer chain, which drives the movement of polaron along the chain direction. In order to study long time movement of the polaron, we adopt the periodic boundary condition.

The Hamiltonian of organic semiconductors includes two parts lattice part and electronic part.

\[ H = H_e + H_{\text{lattice}} \]  

(8)

The electronic part of the Hamiltonian is expressed as the following form because of the existence of the driven electric field:

\[ H_e = H_{\text{SSH}} + H_{so} \]  

(9)

\[ H_{\text{SSH}} = -\sum_{n,\mu} \left[ t_0 - \alpha (u_{n+1} - u_n) - (-1)^{\mu} t_e \right] \left( e^{-i\gamma A} C_{n+1,\mu} + e^{i\gamma A} C_{n,\mu} \right) \]  

(10)

\[ H_{so} = -t_{so} \sum_n \left[ e^{-i\gamma A} C_{n+1,\uparrow} C_{n,\downarrow} - e^{-i\gamma A} C_{n+1,\downarrow} C_{n,\uparrow} + e^{i\gamma A} C_{n,\uparrow} C_{n+1,\downarrow} - e^{i\gamma A} C_{n+1,\downarrow} C_{n,\uparrow} \right] \]  

(11)

Driving electric field is introduced in the form of the index terms of transition integrals, in which \( \gamma = \frac{ea}{\hbar c} \), \( a, e, c \) are the lattice constant, the electronic quantity and the speed of light respectively. \( A \) is vector-potential, which is a scalar in the one dimensional system, and \( A = A(t) \). The driven electric field is \( E(t) = -\partial_t A(t)/c \).

The Hamiltonian of the lattice is expressed in a classical way:

\[ H_{\text{lattice}} = \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n u_n^2 \]  

(12)

in which \( M \) is the effective mass of the lattice point, and \( K \) represents the elastic coefficient of crystal lattice.

Electron wave function \( \Phi_{\mu}(t) \) satisfies the time-dependent Schrödinger equation:

\[ i\hbar \frac{\partial \Phi_{\mu}(t)}{\partial t} = H_e \Phi_{\mu}(t) = (H_{so} + H_{\text{SSH}}) \Phi_{\mu}(t) \]  

(13)

We can get:

\[ i\hbar \dot{\Phi}_{\mu,\uparrow}(n,t) = -t_{n,n+1}e^{i\rho A}(n+1,t) - t_{n-1,n}e^{-i\rho A}(n-1,t) \]

\[ + t_{so}(e^{-i\rho A}(n-1,t) - e^{i\rho A}(n+1,t)) \]  

(14a)
\[ i \hbar \dot{\varphi}_{\mu, \uparrow}(n,t) = -t_{n,n+1}e^{i\varphi_{\mu, \uparrow}}(n+1,t) - t_{n-1,n}e^{-i\varphi_{\mu, \uparrow}}(n-1,t) - t_{SO}(e^{-i\varphi_{\mu, \uparrow}}(n-1,t) - e^{i\varphi_{\mu, \uparrow}}(n+1,t)) \]

\[ (1b) \]

The evolution of the lattice shape of the polymer \( \{ u_n \} \) is determined by the classical equation of motion:

\[ M \ddot{u}_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[e^{i\varphi}(\rho_{n,n+1}(t) - \rho_{n-1,n}(t)) + c.c.], \]

\[ (15) \]

in which density matrix elements in the Equation (15) are determined by the following two equation:

\[ \rho_{n,n'}^s(t) = \sum_{\mu} \psi_{\mu,s}^*(n,t)f_{\mu} \psi_{\mu,s}(n',t) \]

\[ (16) \]

\[ \rho_{n,n'}(t) = \rho_{n,n'}^s(t) + \rho_{n,n'}^{\uparrow}(t) \]

\[ (17) \]

in which \( f_{\mu} \) is the time independent distribution function (Fermi distribution function), which is determined by the occupied state \( (0\text{ or }1) \) of the initial moment.

The electron wave function of initial moment

\[ \Phi_{\mu}(t = 0) = \begin{pmatrix} \Phi_{\mu, \uparrow}(t = 0) \\ \Phi_{\mu, \downarrow}(t = 0) \end{pmatrix} = \begin{pmatrix} \phi_{\mu, \uparrow}(n,t = 0) \\ \phi_{\mu, \downarrow}(n,t = 0) \end{pmatrix} \]

is obtained by solving the Schrödinger equation in the moment \( t = 0 \):

\[ H_{\mu}(t = 0)\Phi_{\mu}(t = 0) = \epsilon_{\mu}(t = 0)\Phi_{\mu}(t = 0) \]

\[ (18) \]

We can get:

\[ \epsilon_{\mu}\phi_{\mu, \uparrow}(t = 0,n) = -t_{n-1,n}\phi_{\mu, \uparrow}(t = 0,n-1) - t_{n,n+1}\phi_{\mu, \uparrow}(t = 0,n+1) + t_{SO}(\phi_{\mu, \downarrow}(t = 0,n-1) - \phi_{\mu, \downarrow}(t = 0,n+1)) \]

\[ (19a) \]

\[ \epsilon_{\mu}\phi_{\mu, \downarrow}(t = 0,n) = -t_{n-1,n}\phi_{\mu, \downarrow}(t = 0,n-1) - t_{n,n+1}\phi_{\mu, \downarrow}(t = 0,n+1) - t_{SO}(\phi_{\mu, \uparrow}(t = 0,n-1) - \phi_{\mu, \uparrow}(t = 0,n+1)) \]

\[ (19b) \]

Before the addition of driving electric field in the one dimensional organic polymer, the most stable position of the system (the static configuration of a polaron) is obtained by the energy optimization:

\[ u_n = \frac{1}{2} \left[ u_{n+1} + u_{n-1} + \frac{2\alpha}{K} \sum_{\mu,s} (\psi_{\mu,s}(n+1,t=0)\psi_{\mu,s}(n,t=0) - \psi_{\mu,s}(n,t=0)\psi_{\mu,s}(n-1,t=0)) \right] \]

\[ (20) \]

The static configuration of a polaron is the initial configuration of the evolution of lattice dynamics, in which \( \sum_{\mu,s} \) describes the sum of the occupied states of the electron. Self-consistent Equation (14) and (15) are obtained through 8 order Runge-Kutta method [20].

One dimensional organic polymer chain is composed of 100 CH groups \( (N=100) \). Preferences [21]:

\[ a = 1.22 \ \text{Å}, \quad \alpha = 4.1eV/\text{Å}, \quad M = 1349.1 eV \cdot \text{fs}^2/\text{Å}^2, \quad t_0 = 2.5eV, \quad K = 21eV/\text{Å}^2, \quad t_e = 0.05eV, \quad t_{so} = 0.02eV \] (This value is a small amount compared to the other interactions).
According to the linear distribution in the calculation the driven electric field is applied, i.e. when time \(0 < t < t_c\), \(E(t) = \left(\frac{E_0}{t_c}\right) \cdot t\); when \(t \geq t_c\), \(E(t) = E_0\), in which \(t_c\) is the starting period of electric field, \(t_c = 30\) fs. Suppose that the driven electric field points to the \(-\hat{x}\) direction, then polaron will move along the \(\hat{x}\) direction. The driven electric field \(E_0 = 5 \times 10^3\) V/cm, which is far less than polaron dissociation field. The driven electric field will reach the maximum value when \(t = t_c = 30\) fs.

If spin-orbit interaction is not considered, i.e. the Rashba electric field is not added, when \(t_{SO} = 0\), the polaron spin will remain constant, which is moving along the \(x\) direction under the effect of the driven electric field. Spin evolution \(S_n^Z(t) = \frac{1}{2} \left(\rho_{n,n}^s(t) - \rho_{n,n}^i(t)\right)\) is shown in the Figure 1.

![Figure 1. The evolution of spin polaron without spin-orbit interaction.](image)

When the Rashba electric field is added \((t_{SO} = 0.02)\), we find spin evolution has changed with the polaron motion, as shown in the Figure 2. The black part is the projection of the spin down (along \(-\hat{z}\) axis direction) and the white part is the projection of the spin up (along \(\hat{z}\) axis direction) in the Figure 2. Obviously, the spin of polaron is precessing. As time goes on, the spin projection in the \(\hat{z}\) axis direction gradually becomes dark. At the time \(t \approx 5000\) fs, the spin projection has been completely black, which indicates that the spin projection of the \(\hat{z}\) axis is downward, soon after the spin projection slowly turns to light. When the driven electric field remains unchanged, the movement velocity of the polaron remains unchanged, which is irrelevant to the Rashba electric field (spin-orbit coupling).

![Figure 2. The evolution of spin polaron with spin-orbit interaction \((t_{SO} = 0.02eV)\).](image)
4. Conclusion
The effect of spin-orbit coupling on one dimensional organic polymer is calculated theoretically. Spin-orbit coupling makes the energy splitting of organic polymers split, but does not erase the spin merger. Due to the weak spin-orbit coupling in organic matter, the band structure of the whole system does not change significantly. When polaron is moving along the one dimensional organic polymer chain under the impact of driven electric field, the spin-orbit coupling interaction can lead to the spin precession. When the driven electric field remains unchanged, the movement velocity of the polaron remains unchanged, and it has nothing to do with the Rashba electric field ($I_{SO}$). This paper theoretically proves that it is feasible to control the spin precession of polaron in organic polymers by the use of external electric field.

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