

Zener tunneling in one-dimensional organic semiconductors

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Abstract

Tunneling effect in one-dimensional organic semiconductors in the presence of an external electric field is studied within the framework of a tight-binding model and a nonadiabatic dynamical method. It is found that under a high electric field, electrons can transit from the valence band (VB) to the conduction band (CB), which is demonstrated to be Zener tunneling in organic semiconductors. The results also indicate a field-induced insulator–metal transition accompanied by the vanishing of the energy gap. It is found that, after the field is turned off, the Peierls phase cannot be recovered.

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1. Introduction

For about three decades conjugated polymers have been attracting considerable interest both in theory and experiment due to their unusual physics properties and potential applications [1–3]. In conjugated polymers there exists strong coupling between electrons and lattice atoms, which induces a single-double bond alternation and an energy gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) [4]. Such kind of Peierls instability contributes to the low conductance of the system. It has been generally accepted that one-dimensional conjugated polymers belong to the family of organic semiconductors (OSEs). The OSEs share some common properties with inorganic semiconductors [5], although the predominant carriers in these two materials are different. The issue of high-field transport in solids is of great concern and has been investigated for many decades due to the basic interest in the physical phenom-

ena involved and many important applications. Early theoretical contributions were made by Bloch and Zener in 1930s [6,7]. It was shown by Bloch that electrons in a periodic lattice potential subject to a high electric field perform temporal and spatial oscillations—Bloch oscillations (BO) [6]. Recently, Bloch oscillations in a one-dimensional organic lattice was investigated in detail by Li et al. [8]. It was found that an electron derived from a dissociated polaron at a high electric field propagates in the form of a free-like electron and performs BO with a net forward displacement in the direction of the field. Based on Bloch's work, Zener further demonstrated that tunneling between Bloch bands is possible at a sufficiently high electric field (Zener tunneling) [7]. Since Zener explained the electrical breakdown of solid dielectric in terms of interband tunneling, the phenomenon of Zener tunneling has attracted considerable interest, particularly in modern nanoscale devices. A large amount of studies have been devoted to its application in various physical systems, such as current-driven Josephson junctions [9,10], atoms in an accelerating optical lattices [11], and field-driven superlattices [12]. It was also explored in a series of experiments [13–15]. To the best of our knowledge, Zener tunneling in organic semiconductors is rarely referred to. In this Letter,

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we consider the dynamical evolution of electronic states in a conjugated polymer chain under a high electric field, and try to explore the possible Zener tunneling effect in organic semiconductors.

2. Model and methodology

The well-known Su–Schrieffer–Heeger (SSH) model is adopted to describe the quasi-one-dimensional polyacetylene (PA) chain. The model which involves primarily electron–lattice interactions has been widely used for studying the properties in PA. The Hamiltonian is expressed as

$$H = H_{\text{ele}} + H_{\text{lat}} + H_{\text{fie}}. \quad (1)$$

H_{ele} refers to the electronic part

$$H_{\text{ele}} = - \sum_n t_{n,n+1} (c_n^+ c_{n+1} + c_{n+1}^+ c_n), \quad (2)$$

where $t_{n,n+1} = [t_0 - \alpha(u_{n+1} - u_n)]$ is the hopping integral of π electrons between sites n and $n + 1$, α represents the electron–lattice coupling constant, u_n is the monomer displacement of site n , and c_n^+ (c_n) denotes the creation (annihilation) operator of an electron at site n . The internal electron–electron interactions are neglected. It has been predicted that the electron–lattice interactions dominate the properties of the polymer [16].

The polymer lattice is treated as

$$H_{\text{lat}} = \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \left(\frac{\partial u_n}{\partial t} \right)^2, \quad (3)$$

where K is the elastic constant and M is the mass of a CH group.

The contribution from the external field is

$$H_{\text{fie}} = |e|E(t) \sum_n (na + u_n)(c_n^+ c_n - 1), \quad (4)$$

where e is the electronic charge and a is the lattice constant. To avoid the drastic vibration of lattice atoms, the electric field $E(t)$ is applied with a linear function $E_0 t/t_c$. After $t = t_c$, the electric field keeps constant as E_0 . A similar smooth way is also adopted when the electric field is turned off. Here $t_c = 100$ fs for all the calculations presented below.

In the absence of the external electric field, the static structure or the initial conditions are determined by minimizing the total energy of the system. In the presence of the electric field, the evolution of the system is traced through the equation of motion of electronic state $\Psi_v(n, t)$

$$i\hbar \frac{\partial}{\partial t} \Psi_v(n, t) = -t_{n,n+1} \Psi_v(n+1, t) - t_{n-1,n} \Psi_v(n-1, t) + eE(t)(na + u_n) \Psi_v(n, t), \quad (5)$$

and the equation of motion of lattice displacement u_n

$$M\ddot{u}_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + 2\alpha[\rho_{n,n+1}(t) - \rho_{n,n-1}(t)] + eE(t)[\rho_{n,n}(t) - 1] - \lambda\dot{u}_n(t), \quad (6)$$

where the element of the density matrix is defined as

$$\rho_{n,n'} = \sum_v \Psi_v^*(n, t) f_v \Psi_v(n', t). \quad (7)$$

f_v is the time-independent distribution function depending on the initial occupation (being 0, 1, or 2). The last term in Eq. (6) is a viscous damping term describing the heat dissipation to the surrounding medium, where the damping parameter λ can be adjusted to get a desired damping.

For any given time, electronic state $\Psi_v(n, t)$ may be expanded on the basis of the instantaneous eigenstates

$$\Psi_v(n, t) = \sum_\mu C_{v,\mu}(t) \phi_\mu(n, t), \quad (8)$$

and $\phi_\mu(n, t)$ satisfies the instantaneous eigen-equation at time t

$$H_{\text{ele}}(t) \phi_\mu(n, t) = \varepsilon_\mu(t) \phi_\mu(n, t). \quad (9)$$

For our study, it is convenient to present the electronic distribution among the instantaneous eigenstates, which is,

$$n_\mu(t) = \sum_v |C_{v,\mu}(t)|^2. \quad (10)$$

Different from the adiabatic dynamics with a fixed occupation, the electronic distribution among the instantaneous eigenstates may be changeable. The above coupled differential equations (5) and (6) are solved by the Runge–Kutta method of order eight with step size control.

3. Results and discussion

In this section, we present the results of electron tunneling in a one-dimensional conjugated polymer chain. The value of the parameters in the Hamiltonian is chosen as those generally used for PA: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å², $a = 1.22$ Å, $M = 1349.14$ eV fs²/Å² [8]. Considering a neutral conjugated polymer chain with 80 monomers, 80π electrons doubly occupy the 40 levels of the valence band and the conduction band is empty. We take the perfectly dimerized configuration as the initial condition. The external electric field is applied smoothly. It arrives at an amplitude value of $E = 35$ mV/Å at $t = 100$ fs and then keeps constant. Soon after the electric field is turned on, polarized charges appear due to the strong electric field. The time dependence of the polarized charges is displayed in Fig. 1, where the solid line presents the total charges distributed in the left half of the chain, and the dotted line presents those in the right half. We find that it takes about 500 fs for the system to reach a dynamical balance. At the present electric field, the amount of the polarized charges is about 5 e. Similar studies for a number of different strengths of the electric fields are also performed, and it is found that the amount of the polarized charges increases with the enhancement of the electric field. Once the electric field is turned off, the polarized charges vanish rapidly.

We now turn to the occupation number n_μ of the instantaneous eigenstate $|\phi_\mu(t)\rangle$. Fig. 2 shows the change of the occupation of instantaneous eigenstates $|\phi_{40}(t)\rangle$ and $|\phi_{41}(t)\rangle$, which are influenced by the electric field more sensitively than the

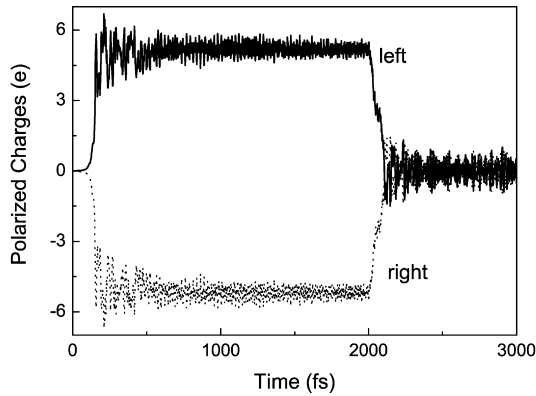


Fig. 1. Time evolution of polarized charges of the left half chain (thick solid line) and the right half chain (thin dotted line) in the presence of the electric field $E = 35 \text{ mV/\AA}$.

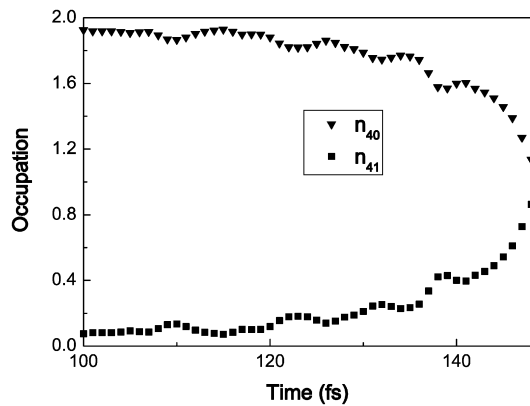


Fig. 2. Occupation numbers of eigenstates $|\phi_{40}(t)\rangle$ and $|\phi_{41}(t)\rangle$ from $t = 100 \text{ fs}$ to $t = 150 \text{ fs}$. The applied electric field is $E = 35 \text{ mV/\AA}$. The triangle indicates the occupation number of eigenstate $|\phi_{40}(t)\rangle$ and the square indicates the occupation number of eigenstate $|\phi_{41}(t)\rangle$.

other instantaneous eigenstates. For $|\phi_{41}(t)\rangle$, which is the instantaneous eigenstate corresponding to the bottom level of the conduction band, it is empty at the beginning. Electrons in the valence band begin to transfer to $|\phi_{41}(t)\rangle$ at about $t = 140 \text{ fs}$. Meanwhile, it is found that the occupation number of $|\phi_{40}(t)\rangle$ is reduced. It can be speculated that the electron transition to $|\phi_{41}(t)\rangle$ is thoroughly contributed from $|\phi_{40}(t)\rangle$ due to the fact that during this time the occupation of the other instantaneous eigenstates keeps unchanged. The charge transfer from the valence band to the conduction band is identified as Zener tunneling. With the increase of time, more instantaneous eigenstates participate in the electron transition, and therefore more and more electrons tunnel from the valence band to the conduction band. The time dependence of the occupation of all the instantaneous eigenstates is depicted in Fig. 3. White and black in the figure indicate a zero and a full occupation, respectively, and gray a partial occupation. At the present field, we find that electron tunneling mainly occurs among instantaneous eigenstates from $|\phi_{31}(t)\rangle$ to $|\phi_{50}(t)\rangle$. For higher electric fields, more eigenstates will be involved into the electron transition. When the system reaches a dynamical balance, the occupation nearly becomes fixed without large fluctuation. Once the field

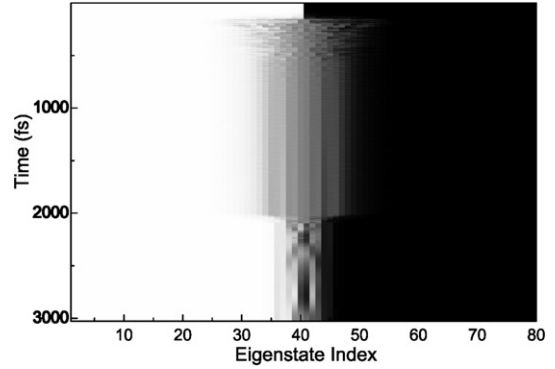


Fig. 3. Time evolution of occupation numbers of all the instantaneous eigenstates. The applied electric field is $E = 35 \text{ mV/\AA}$.

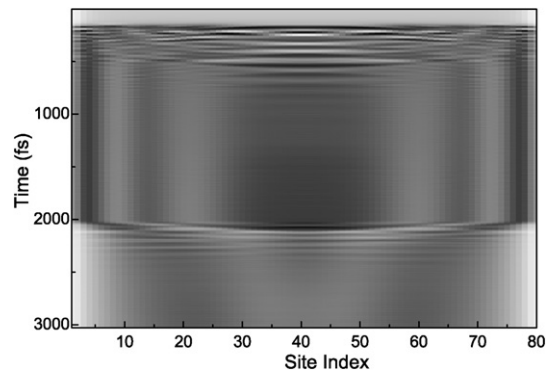


Fig. 4. Time dependence of the lattice configuration $y_n \equiv (-1)^n(2u_n - u_{n-1} - u_{n+1})/4$. The applied electric field is $E = 35 \text{ mV/\AA}$.

is removed, partial electrons will relax from high levels to low levels. The threshold electric field for electron tunneling to occur is about 32 mV/\AA , below which no tunneling is observed.

Fig. 4 shows the time dependence of the lattice configuration ($y_n \equiv (-1)^n(2u_n - u_{n-1} - u_{n+1})/4$) at the present field. Before $t = 140 \text{ fs}$, there is no polarized charge distribution and the lattice configuration keeps its perfectly dimerized state characterized by order parameter $y_n = 0.04 \text{ \AA}$. After $t = 140 \text{ fs}$, the electrons near the top of the valence band begin to tunnel into the conduction band and polarized charges appear in the polymer chain. At the same time, the dimerized configuration is destroyed. It is interesting to note that when the field is turned off, the lattice atoms nearly take on a new alignment of equidistant arrangement ($y_n = 0.0 \text{ \AA}$) except the lattice atoms at the chain end.

We can get more information from the time dependence of the instantaneous eigenlevels, which is plotted in Fig. 5. It can be seen clearly that accompanied with Zener tunneling the energy gap disappears. The electric field closes the gap and combines the valence band and the conduction band into one band. About 2 ps later, when the electric field is switched off, the energy gap will not reappear. One can believe that the conjugated polymer chain experiences a phase transition from insulating phase to metallic phase. For comparison, we have also performed simulations for a rigid semiconductor. The results show that in the rigid semiconductor the energy gap can be recovered when the electric field is turned off. The differ-

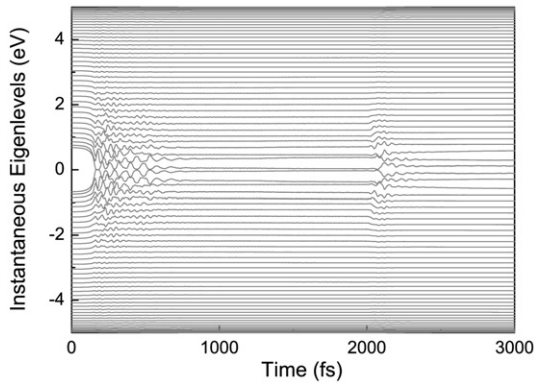


Fig. 5. Time evolution of the instantaneous eigenlevels in the presence of the electric field $E = 35 \text{ mV/\AA}$.

ence between organic semiconductors and rigid semiconductors is ascribed to the ‘softness’ of the organic semiconductor, i.e., strong electron–lattice coupling. The issue of electric field-induced phase transition was first put forward five decades ago by Wannier [17] in the study on possibility of the Zener effect. Recently, the bias-induced insulator–metal transition in a nanoscale metal/OSE/metal sandwich structure based on the SSH model is reported theoretically by Wei et al. [18] motivated by some experimental indications [19,20]. The insulator–metal transition is explained with the energy levels crossover that minimizes the Peierls phase and delocalizes the electron states near the energy gap at the threshold voltage. From our simulation, it can be concluded that a sufficiently high electric field will induce an insulator–metal transition for the conjugated polymers.

4. Summary

In conclusion, we have studied the Zener effect in one-dimensional organic semiconductors under a sufficiently high electric field in the framework of the tight-binding model. The perfectly dimerized configuration of a PA chain with the valence band fully occupied and the conduction band empty is taken as the initial state. Based on a nonadiabatic dynamical

method we find that Zener tunneling occurs in organic semiconductors characterized by the electron transition between the valence band and the conduction band due to the strong field. It is found that the strong electric field minimizes the Peierls phase and makes the energy gap to be zero, i.e., the insulator–metal transition can be realized under a high field. After the field is removed, the Peierls phase cannot be recovered. We also perform simulations for a rigid lattice for comparison, and find that the energy gap reappears after the electric field is turned off. The difference is ascribed to the strong electron–lattice coupling in organic semiconductors.

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References

- [1] J.H. Burroughes, et al., *Nature (London)* 347 (1990) 539.
- [2] S. Datta, W. Tian, *Phys. Rev. B* 55 (1997) R1914.
- [3] W.P. Su, J.R. Schrieffer, A.J. Heeger, *Phys. Rev. Lett.* 42 (1979) 1698.
- [4] R. Peierls, *Quantum Theory of Solids*, Oxford Univ. Press, Oxford, 1955.
- [5] A.J. Heeger, S. Kivelson, J.R. Schrieffer, W.P. Su, *Rev. Mod. Phys.* 60 (1988) 781.
- [6] F. Bloch, *Z. Phys.* 52 (1928) 555.
- [7] C. Zener, *Proc. R. Soc. London* 145 (1934) 523.
- [8] Y. Li, X.J. Liu, et al., *Phys. Rev. B* 74 (2006) 184303.
- [9] K. Mullen, E. Ben-Jacob, Z. Schuss, *Phys. Rev. Lett.* 60 (1988) 1097.
- [10] K. Mullen, et al., *Physica B* 153 (1988) 172.
- [11] M. Jona-Lasinio, *Phys. Rev. Lett.* 91 (2003) 230406.
- [12] K.W. Madison, et al., *Appl. Phys. B: Lasers Opt.* 65 (1997) 693.
- [13] O. Morsch, et al., *Phys. Rev. Lett.* 87 (2001) 140402.
- [14] M. Cristiani, et al., *Phys. Rev. A* 65 (2002) 063612.
- [15] A. Sibille, J.F. Palmier, F. Laruelle, *Phys. Rev. Lett.* 80 (1998) 4506.
- [16] P.B. Miranda, D. Moses, A.J. Heeger, *Phys. Rev. B* 64 (2001) 081201(R).
- [17] G.H. Wannier, *Phys. Rev.* 100 (1955) 1227.
- [18] J.H. Wei, S.J. Xie, L.M. Mei, Y.J. Yan, *Appl. Phys. Lett.* 91 (2007) 022115.
- [19] R. Kumai, Y. Okimoto, Y. Tokura, *Science* 284 (1999) 1645.
- [20] M.M. Matsushita, T. Sugawara, *J. Am. Chem. Soc.* 127 (2005) 12450.