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Magnetoresistance from quenching of spin quantum correlation in organic semiconductors

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ABSTRACT

We present a theory of organic magnetoresistance (OMR) based on the quenching of the quantum correlation between the carrier's spin and its local environment when the incoherent hopping takes place. We prove that this process contributes a spin-dependent prefactor to the attempt-to-escape frequency in the hopping rate, with its value modulated by the magnetic field. The resulting OMR exhibits a positive Lorentzian saturation component and a negative small-field component, which are independent of model parameters. These behaviors, with their isotope effects, are in good agreement with experimental results.

1. Introduction

The organic magnetoresistance (OMR) has attracted much attention since its discovery [1,2], due to its unique features and potential applications in magnetic sensors. It is a sizable (up to 5%) and robust effect under weak magnetic field (tens of milli-Tesla) and room temperature, which is observed in a wide range of amorphous organic semiconductors (OSC) with surprising generality. The OMR behavior can be fitted well by a Lorentzian $\left(B^2/\left(B^2+B_0^2\right)\right)$ or a non-Lorentzian $\left(B^2/(|B|+B_0)^2\right)$ lineshape. The sign of the OMR can be tuned by applied voltage [3,4], device structure [5,6] and temperature [7]. Typically, the electric current increases with magnetic field in bipolar devices [8,9], while decreases in unipolar ones [10]. Recently, efforts have been taken to clarify the isotope effects of OMR, which lead to different conclusions in small-molecule [11] and polymer [12] devices. Another important advance is made by Nguyen et al. with the discovery of an ultrasmall-field component, which scales with the main component and takes an opposite sign [10]. This finding provides more clues on the underlying mechanism of the OMR.

The origin of the OMR is recognized to be the spin interactions in OSC, such as the hyperfine interaction [13] and the spin–orbit coupling [14]. Several microscopic processes have been proposed to be responsible, including the blocking of carriers by bipolarons [15] and excitons [8], interfacial dissociation of excitons [16], and electron–hole pair mediated processes [10,17,18]. Simulations by kinetic Monte Carlo method and stochastic Liouville equations have achieved satisfying comparison with many experimental results. However, it is realized that the observed OMR should be the net effect of multiple components [19,16] from the abundant electronic processes. A comprehensive understanding of the phenomena is still lacking despite much research efforts.

The OMR should stem from the interplay between the dynamics of the charge carriers and that of their spins in OSC. The relative Hamiltonian for the system can be separated into two parts for the charge and the spin. However, their energy scales are distinctly separated. The charge part contains, for example, the transition between different transport sites and the interaction with lattice vibrations. The second part consists of the spin interactions. The dynamics of the former one commonly lie in

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the picoseconds time scale. In contrast, the spin interactions in OSC are in the 0.1 μ eV regime and the related dynamics are coherent in the nanoseconds time scale [23]. Thus most existing theories treat the two parts separately. The charge part renders the incoherent hopping of charge carriers among different localized electronic states assisted by the lattice vibrations. This is distinct from the band transport of extended states in inorganic semiconductors. Phenomenological approach is the most effective tool till now to describe the hopping transport, due to the complexity of the lattice vibrations and the decoherence process. In these works, the transport sites are assumed to have random energies [20]. The hopping rate is given by either the Miller–Abrahams (MA) theory [21] or the Marcus theory [22]. For example, the MA formula for the hopping rate between site i and site j is

$$v_{ij} = \begin{cases} v_e \exp[-(\epsilon_j - \epsilon_i)/k_B T], & \epsilon_j > \epsilon_i, \\ v_e, & \epsilon_j \leqslant \epsilon_i, \end{cases} \quad (1)$$

where v_e is the attempt-to-escape frequency; $\epsilon_j(\epsilon_i)$ is the energy of the electronic states on site j (i); k_B is the Boltzmann constant and T is the temperature. To incorporate the spin dynamics into the above framework, several methods have been proposed, such as the semiclassical [24] approach and the Franck–Condon-like one [25]. Yet in these approaches, the spin-related quantum coherence in the presence of the incoherent hopping is not specifically considered. They are among the essential features of the organic spintronics compared with the traditional ones and worth further study.

In this paper, we focus on the quantum correlation between the carrier's spin and the local environment of spin (LES) formed by the spin interactions. The spin quantum correlation is expected to be quenched by the incoherent hopping of charge carriers. The quenching results in a prefactor η in the attempt-to-escape frequency v_e of Eq. (1). Furthermore, the value of η is determined by the degree of the quantum correlation. By this process, an external magnetic field could influence the hopping rate by modulating the quantum dynamics of the carrier's spin and the LES. As a result, the magnetic field alters the carrier's mobility, which leads to OMR. The paper is organized as follows: Section 2 describes the theory of the OMR from quenching of spin quantum correlations by incoherent hopping of carriers. In Section 3, quantitative results from a hyperfine interaction model are shown. A brief conclusion is drawn in Section 4.

2. Theory

First we present the origin of the prefactor η in the attempt-to-escape frequency. The physical process is illustrated by a two-site model shown in Fig. 1, with a carrier hopping from site i to site j, which is the basic process of charge transport. At time $t = 0$, a charge carrier hops onto site i. When the carrier stays on site i, the interaction with the lattice vibrations will constantly decohere the carrier's dynamics and drive the carrier to make attempts to hop incoherently to site j. Each hopping attempt happens on the decoherence time scale of picoseconds [26].

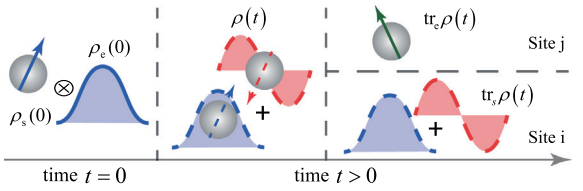

Fig. 1. Illustration of an incoherent hopping process with spin interactions. The carrier's spin is denoted by the arrow and the local environment of spin (LES) by the waveform. The LES can be nuclear spins of hydrogen atoms, etc. At $t = 0$, the quantum state of the composite system is separable; For the hopping attempt at time $t > 0$, the state of the composite system before hopping is quantum-correlated caused by the spin interactions. However, the quantum correlation is quenched by the incoherent hopping to site j and the final state of the composite system is separable again.

Simultaneously, the carrier's spin will interact with the local environment through spin interactions, such as the hyperfine interaction with nuclear spins of the hydrogen atoms. We term the environment as the local environment of spin (LES). The two subsystems of the carrier's spin (ρ_s) and the LES (ρ_e) together constitute the spin-related composite system (ρ) that is concerned in the following. At $t = 0$, the quantum states of the two subsystems are independent, *i.e.*, the density matrix of the composite system ρ is separable as $\rho(0) = \rho_s(0) \otimes \rho_e(0)$. However, for the hopping attempt at time $t > 0$, quantum correlation is generated between them. For the state of the composite system after the hopping, it is noted that the incoherent hopping acts as a local measurement process of the system and will also disturb the spin-related quantum coherence. In such a system, at least three types of coherence can be identified. They include the individual quantum coherence of the two subsystems, which can be reflected by the off-diagonal matrix elements of the reduced density matrix of the carrier's spin/LES $\rho_{s/e}(t) = tr_{e/s}\{\rho(t)\}$, where $tr_{e/s}$ denote the partial trace over the degrees of freedom of the LES/carrier's spin. They are expected to survive the hopping process as the spin interaction is weak. The third type is the quantum correlation between the two subsystems, which is dominated by a different set of off-diagonal density matrix elements [27]. This coherence would be a nonlocal one when the carrier is on site j and therefore it should be quenched after the *incoherent* hopping [28]. To satisfy the above requirements, we use the adiabatic elimination procedure [29]. For the hopping attempt at time t, the initial state density matrix of the composite system is $\rho(t)$ and the final state one is $\rho_s(t) \otimes \rho_e(t)$. According to the Fermi golden rule, this process results in a prefactor $\eta(t)$ in the attempt-to-escape frequency v_e, which reads [30]

$$\eta(t) = tr\{\rho(t)[\rho_s(t) \otimes \rho_e(t)]\}. \quad (2)$$

Further, the value of $\eta(t)$ is determined by the degree of quantum correlation between the carrier's spin and the LES, with larger correlation corresponding to smaller $\eta(t)$ [30]. By this process, an external magnetic field could influence the hopping rate by modulating the quantum dynamics of the composite system. Finally, the phenomenological carrier mobility is magnetic-field dependent.