Understanding magnetic field effects in organic light-emitting devices

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The discovery of magnetic field effects (MFEs) in organic light-emitting devices poses a new challenge for the theoretical studies. Based on the spin-boson theory of magnetotransport that we proposed recently, this article considers various contributions to the MFE. The role of triplet exciton, as an irreducible gradient of the environment in magnetotransport, is discussed extensively. Possible effect of the current caused by secondary charge on the MFE is taken into account to discuss the relation between magnetoresistance and magnetoelectroluminescence. Further experimental correspondence is also discussed.

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1. Introduction

Organic photo-electronic devices, such as light-emitting devices and solar cells, are believed to play an important role in future applications. Among the intrinsic physics of these devices, the dynamics of exciton is essential. Recently, a sizable magnetic field effect (MFE) is found in these devices, including organic magnetoresistance (MR) and magnetoelectroluminescence (MEL), providing a significant tool to understand the spin dynamics of exciton and carrier [1,2]. This interesting effect soon attracted considerable interests [3–18]. Yet, after years of intense research, a theoretical understanding of this MFE is still a challenge. The spin-orbit coupling, which is always the dominating factor in MFE of inorganic materials, is recognized to be invalid in organic materials [3]. On the contrary, the hyperfine interaction (HFI) caused by hydrogen nuclei is then present in many works [4]. Recent experiment on isotope effect on spin response of $\pi$-conjugated polymers verified the importance of HFI [5], while a similar experiment in the Alq3 device showed the response is isotope independent [6], which seemingly indicates that interactions other than HFI may dominate the spin process. A bipolaron model [7] gave a mechanism for both positive and negative OMR at high density of charge carriers. In a word, a comprehensive understanding of the experimental phenomena will be enlightening.

One of the most important issue of MFE is the relationship between MR and MEL. Due to the exactly the same line shapes of the two effects in some experiments, one realized they share the same underlying mechanism [9]. But the experiment on blends of $\pi$-conjugated polymers and fullerenes at various concentrations showed that [10], there are several components of MR and the behavior of MEL and MR shows large difference at some concentration. The difference is originally explained by the mixing of the spin sublevel of electron-hole pair caused by HFI. Yet, since the effect happens under room temperature and low field, it is hard to understand why magnetic field could play a notable role out of so large thermal fluctuation.

Basically, the dynamics of exciton could be divided into several steps: transportation of free carriers, formation of electron-hole pair, transition from loose pair to bound pair (exciton), light-emission of singlet exciton, diffusion, dissociation and decay of other excitons. The intensity of electroluminescence (EL) could be expressed as

$$\text{EL} = \eta I,$$

where $I$ is the charge current and $\eta$ the efficiency of current, which is an effective factor that denote the influence of the scattering between electron and hole. In the case that MEL and MR share the same line shape [11], i.e., the relative change of EL induced by magnetic field is

$$\frac{\Delta \text{EL}}{\text{EL}} = \alpha \frac{\Delta I}{I},$$

it means the efficiency has a power law relation with the current, namely, $\eta \sim I^{-\gamma}$. The case that the magnitude of MEL is larger than that of MR means $\alpha > 1$. On the other hand, in the case the line shape of MEL and MR are not the same, the influence of $\eta$ and $I$ must be considered separately, which is much more complicated.

The paper is organized as follows. In this section, we briefly review the spin-boson theory [12] for the carrier’s transport, and
discuss the former work in detail. In the third section, the influence of some secondary process of current based on the exciton’s dynamics is discussed. The relevance of experiments is given in the discussing section.

2. Magnetotransport

Very recently, we have proposed a spin-boson model to describe the spin interaction between a carrier and the local bosonic environment in an external magnetic field [12]. The Hamiltonian we proposed is,

$$H = \sum_\alpha [\hbar \omega_\alpha b_\alpha^\dagger b_\alpha + \gamma_\alpha (b_\alpha^\dagger b_\alpha)S_z] + g\mu_B B \cdot S$$

(3)

where $S_z$ is the (z-direction) spin operator of a carrier, $b_\alpha$ ($b_\alpha^\dagger$) creates (annihilates) a boson that is the $\alpha$-th mode of the environment, $\omega_\alpha$ the corresponding frequency of bosons, $\gamma_\alpha$ the spin-boson coupling, $B$ the external magnetic field, $g$ the Landé factor that is set to be the commonly accepted value 2.0, $\mu_B$ the Bohr magneton, and $Z$ direction is chosen along that of the specific bosonic mode at each molecule.

In organic materials, the carrier is moving in a complicated environment, which makes the type of charge transport incoherent hopping [19]. Analogously, we could imagine that there is a spin environment that may influence the spin dynamics of carriers. The scale of the coupling from spin environment should be much smaller than that of charge, so that the motion of spin is always coherent during the transport of carrier with one electrode to the other [13]. This spin environment is the response to the MFE in organic materials, and its scale should be the same as the typical applied magnetic field in common MFE.

Since spin-orbit coupling is believed to have little influence [3], HFI was realized to be essential in the spin environment. This is partly because that the typical HFI in organic materials is around several $\mu$eV, which is very close to the Zeeman energy of magnetic field that makes the magnitude of MFE grow quickly [4]. Whereas, HFI caused by hydrogen nuclei in organic molecules is more or less a classical local magnetic field due to the small scale of magnetic field in the system. As we will demonstrate later, only a classical magnetic field can not induce any MFE.

There is another factor that may contribute to the spin environment, that is, triplet exciton. Compared to inorganic light-electronic systems, exciton in organic materials has much longer lifetime, which gives it more opportunity to scatter with carriers and other excitons. Especially, due to selection rule, triplet exciton with spin 1 does not emit light and will keep diffusing in the device for a very long time. Hence, it is natural to consider it as a spin environment, and we use bosons that couple with a quantum spin to describe the effect of this triplet exciton. Recent experiment on the triplet-polaron interaction has found the MFE is linear with EL, i.e., the density of exciton, which demonstrates the dominating role of triplet excitons [20].

Once we have a spin environment that is described by a set of bosons, we could evaluate the intermolecular hopping rate of
carriers via Fermi golden rule [12], i.e., the hopping rate from one molecule to another is expressed as

$$v = \frac{t_j^2}{\hbar} \text{Tr}(\tilde{\rho} \rho(0) \rho(t_w)).$$

(4)

where $\tau$ is the decoherence time within which the hopping is coherent, $J$ the overlap integral of wavefunction $s$ between molecules including all the magnetism independent factors, $\tilde{\rho}$ the density matrix of bosons after the hopping, $\rho(s)$ the density matrix at another molecule with spin $s$, $\rho(t_w)$ the density matrix of the system before hopping with $t_w$, the waiting time of a carrier at one molecule. The detail of the derivation could be found in [12]. Within this expression, we can calculate the magnetic field dependent hopping $\Delta v/s = [(v(8) - v(0))/v(0)]$, which could be directly connected to the experimental measurements of MR.

The physical process of the spin dynamics during carrier’s hopping is shown in Fig. 1. At time $= 0$, the carrier is not entangled with the environment. Right at this moment, the coupling between them is switched on, and the system starts to evolve. Due to the quantum fluctuation of bosons, the carrier’s spin may entangle with them, and in principle, the longer the time evolves and the larger the spin-boson coupling is, the larger the entanglement becomes. Then at time $= t_w$, the carrier will hop out of the entanglement to another molecule. Obviously, the larger the entanglement is, the smaller the hopping rate is. Thus, the key point for MFE is the quantum nature of the bosonic environment.

Fig. 2 shows the mechanism of how magnetic field influence the hopping rate. The choice of parameters is similar to those in [12], which are mainly from corresponding experiments. As we have discussed, the magnitude of hopping rate depends directly on the entanglement, that is, after the time of $t_w$, how large the entanglement could become. When there is no external magnetic field, the carrier’s spin only feels the influence of bosons. While when the magnetic field is very large, the influence of bosons becomes less important. The entanglement in the first case is much larger than that in the second one. Thus, MFE happens, and this is the mechanism for a negative MR. In the present work, we do not discuss the positive MR, which will be our future work. Fig. 3 shows the calculated magnetic field dependent hopping rate under different $t_w$. The basic line shape is very similar to that of MR and the dependence on $t_w$ is clearly shown. Following $t_w$ increasing, the MFE grows quickly. To explain the complicated experimental findings, $t_w$ is an essential factor in the theory, which could be directly related to the experimental parameters, such as mobility, bias voltage, thickness of the device. It is worth noting that, the Lorentzian and non-Lorentzian lineshape of MR could be obtained in the framework of present theory via changing the value of $\gamma$.

Now, an important question is why we need to use the language of quantum fluctuation and entanglement. It is equivalent to ask how the spin dynamics could affect the charge transport. If the spin environment is classical like a hyperfine field, the carrier is an isolated quantum particle, whose charge and spin degree of freedom decouple with each other. In this case, the charge current would never be spin dependent. Therefore, only when a carrier is immersing in a bigger quantum system, i.e., another degree of freedom or an auxiliary part is introduced, the charge current could be related to its spin via some indirect way. For example, in inorganic magnetotransport, a local quantum spin or the orbital angular momentum is always the case. In this work, we realize that the triplet exciton plays the role of an auxiliary quantum partite. Of course, one can use a number of quantum spin to simulate the triplet excitons, but for simplicity, a bosonic environment is more efficient to deal with.

In Fig. 4, the various MR by changing the boson energy is shown. In Fig. 4(a) and (b), we show the cases for different $B_0 (\equiv 2\gamma^2/\hbar g_\gamma B)$, defined as an effective magnetic field induced by the bosons. We find that, at large $\h_0$, the MR vanishes as expected. This is because when the boson energy is large enough, the boson can not be excited to higher energy level, which means the bosonic environment becomes classical. From the perspective of entanglement, it is easy to understand the vanishing MR since a classical field does not entangle with the carrier’s spin. This demonstrates the quantum nature is essential for the MR effect. Meanwhile, MR is nonmonotonicity with $\h_0$, and the peaks are almost the same for a fixed $B_0$. To further study the peaks, we show the curves for various $t_w$ in Fig. 4(c) and (d). The position of the peaks is exactly located at the boson energy that corresponds to the corresponding one of the waiting time. A nearly linear relationship could be found between the boson energy and the inverse of waiting time, which is not shown here.

### 3. Influence of secondary process

When an electron meets a hole, they may go together to generate an exciton. Statistically, the ratio of the generation rate of singlet and triplet exciton is 1:3. But in reality, the situation is quite complicated, and it is not easy to reach this ideal value [21]. The total current $I$ is consist of two parts: conducting charge current $I_1$ from the intermolecular hopping of carriers and the current $I_2$ caused by secondary charges, such as dissociation of excitons, charge reaction between carrier and exciton, scattering among excitons. Hence, $I = I_1 + I_2$.

(5)

If $I_2$ is negligible, i.e., $I_1 \gg I_2$, or $I_2$ is hardly influenced by magnetic field, i.e., $\Delta I_2 \sim 0$, the MFE of $I$ is mainly from $I_1$, which is the case studied in the second section. Only when $I_2$ and $\Delta I_2$ is not negligible, it is then necessary to consider the MFE of secondary charge. Normally, the conducting current $I_1$ is linear with the density of carrier, while $I_2$ is a nonlinear term, which may be contributed by many complicated process as stated above. So a possible experimental way to examine whether the current of secondary charge is important in MFE is to investigate the relationship between current and density of carrier.

If now the current of secondary charge is important, the remaining question is how it becomes magnetic field dependent. Firstly, since singlet excitons carries spin zero, it will not be influenced by magnetic field individually. Thus, people naturally realized that, the interconversion between singlet and triplet exciton [14] or the annihilation of two triplet excitons [15,16] may be the origin of MFE. The physical resource that induces these transitions is recognized to be hyperfine field. Yet, it is hard to understand a classical field could change the total spin of exciton, unless one consider the quantum fluctuation of nuclear spins, which will be a higher order effect. Hence, experiment has found that the intramolecular interconversion rate is magnetic field independent [17].
Even if we do not consider any interconversion, the dynamics of triplet exciton may also be influenced by magnetic field individually, though that of singlet exciton will never be influenced due to its vanishing spin. For example, imagine there is an electron residing in one molecule, and in its two nearest neighbors there are two holes respectively, one of which will form a singlet exciton with the electron and the other is for triplet. If no other factors affect the process, the possibility for the electron to meet each of these two holes is exactly the same. However, when the generation rate of triplet exciton is modulated by magnetic field, the generation rate of singlet may also change, so does EL. This is a simplified picture to depict the possible influence of secondary charge. The detailed investigation will be published in the future.

4. Discussion

In the spin-boson theory, how to determine the spin-boson coupling is the basic issue. As has discussed, triplet-excitons play a basic role in the environment, so this coupling should be strongly dependent on the density of excitons that could be adjusted experimentally in many ways. As we know, recent experiment has found some linear relationship between the saturated MR and intensity of EL from triplet-carrier interaction model [20]. This conclusion coincide with the present theory.

Moreover, another important physical quantity to OMR is the boson energy $\hbar \omega$, which should depend on the constitution of the environment, related to characters of specific material, such as the mass of atoms and/or radicals in the molecule, electronic excitation energies. Due to the nonmonotonicity of OMR on $\hbar \omega$ as shown in Fig. 4, the discrepancy of isotope effect in different materials [5,6] might be understood within the theory. It was also shown [15] experimentally that the OMR is strongly associated with the excitation energy by changing dopants.

In the end, we would like to discuss the temperature dependence of MFE in organic semiconductors. Although there are works considering the MFE at low-temperature [18], the common MFE is robust at room temperature. Normally, at very low-temperature, the type of carrier transport may be extremely different from the one at room temperature. Since the thermal energy that makes the carriers hop out of the binding of the molecule is no longer sufficient when the temperature is low, the hopping transport is not valid. Tunneling between molecules becomes essential in this situation [19]. Thus, the study on low-temperature MFE should be much more difficult and needs more detailed researches. So does the organic spin valve effect [1], which corresponds to the low-temperature injection problem.

5. Conclusion

In summary, we have discussed in detail our former work of spin-boson theory for magnetic field effect in organic semiconducting materials. The discussion is divided into two part: the magnetotransport and the influence of current caused by secondary charge. The first case is based on a coupling between charge carriers’ spin and a local bosonic environment, we discussed the dominating role of triplet exciton in the environment. For the second case, we have qualitatively discussed under what situation the current of secondary charge may function. Corresponding experiments are discussed.

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