A theory for magnetic-field effects of nonmagnetic organic semiconducting materials

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Abstract – A universal mechanism for strong magnetic-field effects of nonmagnetic organic semiconductors is presented. A weak magnetic field (less than hundreds mT) can substantially change the polaron hopping coefficient between two neighboring organic molecules when the two hopping states are not too symmetric. Under the illumination of lights or under a high electric field, the change of hopping coefficients leads also to the change of polaron density so that photocurrent, photoluminescence, electroluminescence, magnetoresistance and electrical-injection current become sensitive to a weak magnetic field. The present investigation indicates a convincing new mechanism for organic magnetic-field effect.

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Introduction. – One of the long-term unsolved fundamental issues in organic physics is the mechanism behind the strong responses of electrical and optical properties of nonmagnetic organic semiconductors to a weak magnetic field, known as organic magnetic-field effect (OMFE) [1–4]. The recent revival of interest in OMFE of the magnetoresistance, photoluminescence, photocurrent, electroluminescence, and electrical-injection current of organic semiconductors is largely due to its importance in fundamental science and technology applications. Firstly, there is a belief that the OMFE can be used as a powerful tool to probe microscopic processes of organic materials. Secondly, the OMFE can be used to develop new multifunctional organic devices [5]. Experiments showed that OMFE has the following surprising yet universal features. 1) The OMFE appears in vast different organic semiconductors without any magnetic elements at room temperature although the possible energy level shifts due to the presence of a magnetic field are orders magnitude smaller than the thermal energy and other energy scales. 2) The electroluminescence, photocurrent, photoluminescence, and electrical-injection current are very sensitive to a weak magnetic field with both positive and negative OMFE though positive OMFE (or negative magnetoresistance (MR) in the convention terminology) at very weak field is typically observed. 3) The OMFE can often be fitted by two empirical formulas: \(B^2/(B^2 + B_0^2)\) and \([B/(B + B_0)]^2\) [6], where \(B\) is the applied external magnetic field. In the theoretical side, the current belief in the community is that the OMFE is intimately tied to spin physics involving spin configuration, spin correlation, and spin flip [4]. However, as the spin related Zeeman energy (\(g\mu_B\vec{S} \cdot \vec{B} \sim 10^{-5}\text{ eV for one tesla}\)) is negligibly smaller than the room-temperature thermal energy \((k_B T \sim 0.026\text{ eV})\), there is no convincing arguments why an extremely small Zeeman energy can beat the thermal energy in controlling electron spin dynamics to generate this OMFE. A possible understanding may be from the dynamic behavior. But up to now, there has had no a theoretical investigation to include the dynamical effects. In this report, we try to understand the OMFE from another route. As it is incomprehensible from energy consideration for OMFE, we wish to understand it from the polaron kinetics. A magnetic field will generate a direct term to the hopping integral of the polaron between two
molecules that in turn changes the conductance. This theory does not explicitly rely on the electron spin degrees of freedom. It is showed that the OMFE may be much more pronounced in an organic semiconductor with a narrow bandwidth and an asymmetry structure.

**Model and formula.** – Organic semiconductors have a few distinct properties that their inorganic counterparts do not have. Firstly, unlike an atom that is sphere-like, an organic molecule is highly irregular. As a result, an organic molecular wave function has no obvious symmetry. Secondly, organic molecules in organic semiconductors are bonded by the Van der Waals force so that their bands are very narrow in comparison with an order of 10 eV bandwidth for their inorganic counterparts, which means that the charged carrier (polaron) is strongly localized [7]. Thirdly, the intramolecular excitons have strong binding energies of the order of eV. On the other hand, an electron and hole become a polaron pair when they are oriented on different molecules because of weak intermolecular binding [4]. The electrical properties of an organic semiconductor are mainly determined by the motion of polarons since the motion of excitons does not contribute to the electric current. The singlet excitons are responsible for the luminescence. A weak field should not change much the energy levels of various excitation states so that their populations at thermal equilibrium are not sensitive to a magnetic field because they depend only on the energy level distribution and temperature. Any significant change in magnetoresistance near the quasiequilibrium state must come from the mobility change. The question is whether a weak field of 100 mT can change the mobility of polarons in organic semiconductors. In a usual inorganic crystals with $s$-like wave function, the answer is no. However, we argue below that this can indeed happen in an organic conjugated material with a highly irregular molecular wave function.

In order to understand why a weak magnetic field can change charge carrier (electron and hole or polaron) mobility in an organic conjugated material, we consider a system with two molecules separated by a distance $d$ as schematically shown in fig. 1.

One-electron Hamiltonian in a magnetic field can in general be described by

$$ H = -\frac{1}{2m} \left( \vec{p} - \frac{e}{c} \vec{A} \right)^2 + V_1 + V_2, $$

where $V_1$ and $V_2$ are the potential created by molecules 1 and 2, respectively. $\vec{A}$ is the vector potential due to magnetic field $\vec{B}$. For simplicity and clarity, we shall assume that the two molecules are aligned along the $x$-direction, the field is along the $z$-direction (pointing out of the paper). The important quantity for electron transport is the tunneling matrix element between two molecules. When an electron tunnels from an initially occupied state, say $\psi_1$ of molecule 1, to the empty state $\psi_2$ of molecule 2 with tunneling matrix $t$, it will contribute to the hopping probability $P$ (per unit time), proportional to $|t|^2 \exp(-\Delta \xi_{12}/k_B T)$, where $\Delta \xi_{12}$ is the energy difference of the two states. The hopping conduction can be regarded as an electron diffusion process with a diffusion constant $D = \mu d^2$, where $d$ is the average distance between two neighboring molecules. According to the Einstein relation, the electron mobility $\mu$ is given by $\mu = eD/k_B T$, which is related to the conductivity in the conventional way [8]. Therefore, we can concentrate on how the tunneling matrix element depends on the magnetic field in order to study the magnetoresistance of the system.

In the tight-binding approximation, one of the authors in an early publication has generalized Bardeen’s transfer matrix formalism to high dimension and in the presence of a magnetic field [9]. In 3D, it is

$$ t = \frac{\hbar^2}{m} \int \left[ \psi_1^* \frac{\partial \psi_2}{\partial x} - \psi_2 \frac{\partial \psi_1^*}{\partial x} \right] \frac{2i}{\phi_0} (\vec{A} \cdot \hat{r}) \psi_1^* \psi_2 \right|_{x=d/2} dy dz, $$

where $\phi_0 = e \hbar / c$ is the flux quanta. For small $\vec{A}$ when the magnetic length $l_B = \sqrt{\phi_0 / B}$ is bigger than $d$, magnetic confinement that is responsible for the exponential increase of resistance in the usual hopping conduction can be neglected and $\psi_1$ and $\psi_2$ do not depend on $B$ to the zeroth-order approximation. Then the magnitude of the field-independent part of $t$ is of the order of

$$ t_0 = \frac{\hbar^2}{m \xi} \int \psi_1^* \psi_2 \big|_{x=d/2} dy dz, $$

while that of the field-dependent part is

$$ t_B = \frac{\hbar^2}{m l_B^2} \int y \psi_1^* \psi_2 \big|_{x=d/2} dy dz, $$

where $\xi^{-1} = \xi_2^{-1} + \xi_1^{-1}$, and $\xi_1$ and $\xi_2$ are the localization lengths of $\psi_1$ and $\psi_2$, respectively. Both terms depend

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**Fig. 1:** Schematical draw of two organic molecules (Alk$_3$) separated by a distance $d$ and aligned along the $z$-direction. Molecule 1 is centered at the origin, and molecule 2 is centered at $(d, 0, 0)$. The field is assumed to be along the $z$-direction. $\psi_1$ and $\psi_2$ are two localized states with localization lengths $\xi_1$ and $\xi_2$, respectively.
on the nature of the wave functions. This explains why the OMFE value varies from sample to sample, and from material to material [4]. The second term vanishes for s-like wave function. This is why the corresponding effect does not show up in usual inorganic semiconductors. Due to the irregular structures of organic molecules, one will expect an appreciable value for the second term, resulting in a sizable change of the hopping probability.

**Calculation and discussion.** – To give an estimate of the magnetic-field–dependent part $t_B$, we consider a small molecule with an asymmetric 3D square-well model. Numerical calculation shows, for a magnetic field of 1 tesla, $t_B/t_0 \sim 10^{-3}$, which seems to be too small to create an apparent OMFE. But for an asymmetric 3D harmonic model, our calculation gives $t_B/t_0 \sim 0.1$, which is comparable to the observed OMR value of 1–10%. Therefore, in some organic semiconductors, a weak magnetic field can apparently affect the hopping of electrons from one molecule to another and so create an observable OMFE. It should be mentioned that the above deduction is only based on a weak-field approximation. For a stronger magnetic field, we have to consider an exact solution of the electronic state in the presence of the field, and in that case it is expected that the effect should be more apparent and in that case the spin-related Zeeman effect should be also included.

Due to the Van der Waals bonding, the OMFE is measurable only under an optical injection of carriers or an electric carrier injection by an electric field above a threshold. When an organic semiconductor is under the illumination of a light or under a high electric field, the field-dependent $t$ results in a field dependence of polaron density. Take optical injection of carriers as an example, under the illumination of a light, an electron in a highest occupied molecular orbit (HOMO) absorbs a photon and jumps to a higher empty molecular orbit of the same molecule. As schematically illustrated in fig. 2, the excited electron can either dump its excessive kinetic energy to its environment and form an exciton with the hole left behind or jump to neighboring molecules and become a polaron. Depending on the relative probabilities of excited electrons (holes) staying in the same molecules and jumping to different molecules, the polaron density shall vary with the illumination intensity. Let us denote the probability (per unit time) for a pair of electron and hole on the same molecule to form an exciton by $P_o \sim \hbar/\tau$, where $\tau$ is the typical time for a pair of electron and hole to form an exciton. $P_o$ is not sensitive to a weak field since the field cannot change much molecular orbits that determine $P_o$. Then the polaron generation rate per unit volume is $J P/(P_o + P)$, where $J$ is the photon absorption rate per unit volume and $P \propto |t|^2$ is the intermolecular hopping probability.

Without the illumination of a light, the polaron density shall reach its equilibrium density $n_0$ at a rate of $\gamma(n - n_0)$, where $\gamma$ is the polaron decay rate. At balance, $J P/(P_o + P) = \gamma(n - n_0)$, thus the photon-generated polaron density should be $n = n_0 + J P/[\gamma(P_o + P)]$. Clearly, the $B$-dependence of $P$ results in a $B$-dependence of the polaron density.

Since the OMFE can often be fitted by two empirical functions $B^2/(B^2 + B_0^2)$ and $[B/(B + B_0)]^2$ [6], let us consider it with the present theory. According to eq. (2), $t$ takes a form of $B_0 + iaB$ with $B_0$ and $a$ a real and field-independent parameters if $\psi_1$ and $\psi_2$ are real functions. This is the case when the molecule orbits involved in hopping are localized or not degenerated [10]. In this case, $P \propto |t|^2 = a(B^2 + B_0^2)$ and the polaron density shall depend on the magnetic field as $n = n_0 + J P/\gamma(P_o + P) = n_0 + \alpha B^2/(B^2 + B_0^2)$, where $n_0$, $n_0'$, $\alpha$ and $B_0$ are $B$-independent parameters that depend on the molecule orbits involved. Thus, $B^2/(B^2 + B_0^2)$ is a natural OMFE function for $t = B_0 + iaB$. Interestingly, this function also appears in the magnetization expectation value involving hyperfine interactions when only quantum spin precession is considered and all other processes are neglected [11,12]. However, it is puzzling to us how one relates the $z$-component spin to the resistance and how the spin polarization can survive under the huge thermal interaction. Surprisingly, the second type of empirical function appears naturally for $t = i(B_0 + aB)$. According to eq. (2), this can happen when the spatial derivatives of $\psi_1$ and $\psi_2$ are functions multiplied by pure imaginary numbers. Of course, this must correspond to degenerated states. In this case, the leading term in the polaron density takes the form $[B/(B + B_0)]^2$ in a similar argument when $P \gg P_0$. In reality, electron (polaron) hopping between two organic molecules should involve many molecule orbits, especially in photophysical processes and in a high electric field. One then needs to add contributions from all hopping events. Thus, it is likely that both $B^2/(B^2 + B_0^2)$ and $[B/(B + B_0)]^2$ processes are present, and OMFE should then be fitted by the linear combinations of these two functions, consistent with experimental

![Fig. 2: Schematic illustration of polaron and exciton formation after a pair of electron and hole is created by photon absorption. An excited electron has probability $P$ to jump to the neighboring molecules to form free polarons, and probability $P_0$ to form an exciton with a hole.](image)
findings. In this theory, $B_0$ is determined by $t_0$ and the direct field term $t_B$. For an organic semiconductor, $t_0$ is from the Van der Waals force whose value should be mainly controlled by the C-H bonding group inside the organic molecule. Thus, we believe that $B_0$ may vary from one sample to another, its value should not be too sensitive for different materials. There are some experimental investigations with different organic semiconductors to check the universality of OMAR [13–15]. Indeed, Martin et al. recently studied the magnetoresistance for organic semiconductor devices fabricated with small molecules, oligomers, conjugated polymers and non-conjugated polymers, separately. According to their experimental data, the peak widths (which are related to $B/B_0$ in the present model) are almost the same, insensitive to the specific samples.

The present mechanism is very robust. At room temperature, the transport of charge carriers will involve many different molecule orbits. Each hopping event will be subject to the influence of this mechanism as long as magnetic confinement is negligible ($l_B > d$) and the molecular structure is not sphere-like. Of course, thermal average over all hopping events is needed. Molecule-molecule orientation in organic semiconductors should be quasi-random due to the nature of the organic molecules. A magnetic field can be along any direction with respect to the molecule-molecule bond instead of the perpendicular direction as assumed in the above discussion. This explains why OMFE is not sensitive to the field direction in devices. According to eq. (2), different angle between the field and the molecule-molecule bond leads to different hopping coefficient. It should also be emphasized that the mechanism presented here does not depend on electron spins, and it does not require large energy splits of different spin configurations. It is applicable to both bipolar and hole-only (or electron-only) devices. Differently from the previous theories that try to relate the OMFE to the changes of electron levels, the present theory attributes the OMFE to the change of electron hopping coefficient in a field. Thus, it does not have all the troubles as those spin-dynamics–related theories involving concepts of excitons and bipolarons [6,16–19].

**Conclusion.** In conclusion, we presented a novel mechanism for the OMFE for nonmagnetic organic semiconductors. The mechanism is very general and robust for organic semiconductors, but is normally not important for usual covalently bonded inorganic semiconductors. The mechanism can not only explain all experimentally observed OMFE, but also provide a solid theoretical basis for the empirical OMFE formulas. New experiments are needed to firmly establish this mechanism as the genuine cause of the OMFE.

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