

Monte Carlo simulation of spin correlations in organic semiconductors with an arbitrary relation between hopping rates and spin dynamics

I. V. Tolkachev and Y. M. Beltukov 
Ioffe Institute, 194021 St. Petersburg, Russia

A. V. Shumilin ^{*}
Jozef Stefan Institute, 1000 Ljubljana, Slovenia

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We present a kinetic Monte Carlo (KMC) algorithm designed to study spin correlation phenomena in organic semiconductors including the effect of a magnetic field on electroluminescence and organic magnetoresistance. It allows for an arbitrary relation between hopping rates and spin-precession frequencies, and it incorporates an intermediate averaging procedure to model the spin relaxation within a single KMC simulation run. Our results demonstrate that even a small fraction of hops occurring faster than spin precession can significantly impact the width of the magnetic field dependence of the electroluminescence, which is typically associated with the strength of the hyperfine interaction between electron and nuclear spins.

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I. INTRODUCTION

Organic semiconductors constitute a rapidly evolving class of materials that holds significant promise for enhancing the foundational elements of electronics. While organic light-emitting diodes (OLED) are already widespread, new applications are now in development. Among them are organic solar cells [1], whose efficiency has already surpassed 15% [2], and organic field-effect transistors [3,4], which can be applied as flexible chemical sensors [5]. Beyond their practical applications, these materials exhibit properties of fundamental interest to physics, such as the transient localization transport regime observed in organic semiconductors with exceptionally high mobility [6,7].

Notably, the unusually long spin relaxation times $\gtrsim 10\text{--}100$ ms [8] also make organic semiconductors promising materials for spintronics. The spin phenomena in these materials are very rich and include room-temperature magnetoluminescence [9], strong “organic” magnetoresistance (OMAR) in weak magnetic fields and in room temperature [10,11], and optically detected magnetic resonance [12,13]. While some of these phenomena are already relatively well studied and applied in prototypical magnetic sensors [14–16], the others, such as current noise due to nuclear spin dynamics [17,18] and dynamical polarization [19] of electron spins, are now only predicted.

With all their potential, organic semiconductors remain challenging materials to simulate. A typical organic

semiconductor is an amorphous material composed of small molecules or short polymers. The only possible way to describe it from first principles is with multiscale modeling. In the first step of such modeling, the molecular composition is calculated by molecular-dynamics methods [20]. Then, the electron states, their overlap, and renormalization energies are computed with density functional theory [21,22]. After this, the theory of polaron transfer is applied to calculate the hopping rates [23–25]. At the final stage, the transport properties are studied with either a master equation or the kinetic Monte Carlo (KMC) approach [26,27]. While in some articles [22] the complete multilevel scheme has been successfully applied, all of its components require further development.

This article is focused on incorporating the spin phenomena into the final stage of the calculations, when intermolecular hopping rates are already known and macroscopic transport properties are studied. There are two competing methods at this point: master equations and KMC. Although master equations are generally more efficient when applicable, addressing organic spin phenomena necessitates including spin correlations into the set of equations [28,29]. While the correlation master equation method is currently under development [30–34], it is known that sometimes a very large number of correlations are required to reliably describe the spin transport [29]. Furthermore, the master equation method is less general and often fails when Coulomb interaction between charge carriers is strong. In these scenarios, KMC simulations are required.

The method of introducing spin correlations in KMC is developed in [35] for the case when electron hops are slow compared to spin precession. However, the existing *ab initio* simulations [22] show that although this assumption holds true for a significant portion of the hops, the distribution of hopping rates is exponentially broad, and some hops occur faster than spin precession. This part of the hops can be larger

^{*}Contact author: andrei.shumilin@ijs.si

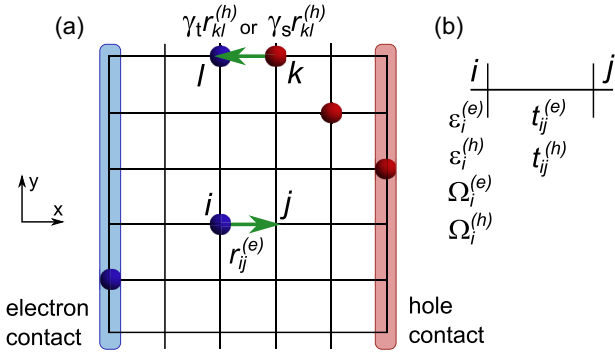


FIG. 1. (a) The model of an organic semiconductor. (b) The values ascribed to each site i and each pair of neighbor sites ij .

than $\sim 25\%$ at least in certain cases. Additionally, some experiments show very long spin diffusion lengths (up to 100 nm) in organic semiconductor devices [36–38], which also challenges the assumption of slow hops and fast spin precession.

In this article, we present a KMC approach to spin phenomena in organic semiconductors that allows an arbitrary relation between hopping rates and spin-precession frequencies. The article is organized as follows. In Sec. II, we discuss the model of organic semiconductor and the common Monte Carlo algorithm that could be used for its modeling if the spin correlations were irrelevant. In Sec. III, we define the spin correlations, and we show how they can be incorporated into the Monte Carlo simulation. In Sec. IV, we describe the procedure of intermediate averaging that allows spin correlations to relax during a single realization of the Monte Carlo algorithm. In Sec. V, we show the results of our calculations in several scenarios. In Sec. VI, we present a general discussion of our results.

II. MODEL AND MONTE CARLO ALGORITHM

In this section, we initiate the discussion on our KMC model of organic semiconductors. Initially, we present a simplified version of the algorithm, omitting electron or hole spins, to facilitate understanding. However, we provide some details essential for the subsequent integration of spin degrees of freedom. This integration, required to study the exciton mechanism of OMAR and magnetoelectroluminescence in OLEDs [39], which is our main point of interest, is made in Sec. III.

We consider an organic material composed of small molecules providing transport for both electrons and holes, as in the case for the OLEDs based on tris(8-hydroxyquinoline) aluminium (Alq3) [40]. The transport arises from the electron hops over the lowest unoccupied molecular orbitals (LUMO) and hole hops over the highest occupied molecular orbitals (HOMO). When both an electron and a hole appear on a single molecule, they form a singlet or a triplet exciton. These excitons can recombine either radiatively or nonradiatively. The exciton binding energy is usually comparable to 1 eV [41], preventing their dissociation.

We consider numerical samples (see Fig. 1) with a square lattice where each site i of the lattice corresponds to a molecule in an organic semiconductor. The energy of its

LUMO equals $\varepsilon_i^{(e)}$ and the energy of its HOMO equals $\varepsilon_i^{(h)}$. When an electron or a hole is present on the molecule, the hyperfine interaction with nuclear spins and the external magnetic field lead to the precession of its spin [42]. Many molecules commonly used in OLEDs contain ten or more hydrogen atoms with nuclear spins (for instance, Alq3 has 18 such atoms), resulting in a large number of nuclear spins interacting with a single electron spin. It allows us to describe the hyperfine interaction as an effective Overhauser field acting on electron and hole spins. Correspondingly, we introduce the frequencies $\Omega_i^{(e)}$ and $\Omega_i^{(h)}$ of electron and hole spin precession in zero magnetic field, respectively. We assume $\Omega_i^{(e)}$ to be different from $\Omega_i^{(h)}$ because the hyperfine interaction with nuclear spins on various atoms is different for electrons in LUMO and holes in HOMO. In this article they are considered to be independent, and both of them are described by the normal distribution with the density $\propto \exp(-|\Omega_i^{(e,h)}|/2\Delta^2)$. Here $\hbar\Delta \sim 10^{-6}$ eV is a typical energy of the hyperfine interaction of electron and nuclear spins. The frequencies $\Omega_i^{(e)}$ and $\Omega_i^{(h)}$ are conserved during the simulation. In an external magnetic field, $\mu_b g \mathbf{B}/\hbar$ is added to all the frequencies $\Omega_i^{(e)}$ and $\Omega_i^{(h)}$. Here μ_b is the Bohr magneton, $\mathbf{B}$ is the external magnetic field, and $g = 2$ is a g -factor that is considered to be equal for electrons and holes because of the small spin-orbit interaction in typical organic semiconductors.

Organic semiconductors are usually strongly disordered due to random energies of HOMO and LUMO ~ 0.1 eV [43,44] and a broad distribution of overlap integrals between neighbor molecules [21]. It leads to a hopping nature of transport with electrons and holes making noncoherent hops between neighbor molecular orbitals. The hopping rates $r_{ij}^{(e,h)}$ can be expressed with the equation

$$r_{ij}^{(e,h)} = \gamma_{ij} \exp \frac{\varepsilon_{ij}^{(e,h)}}{2T}, \quad (1)$$

where $r_{ij}^{(e)}$ is the rate of electron hops from site i to site j , T is the temperature, and $\varepsilon_{ij}^{(e)} = \varepsilon_i^{(e)} - \varepsilon_j^{(e)}$ is the difference between electron energies on sites i and j , respectively. γ_{ij} depends only on the absolute value of $\varepsilon_{ij}^{(e,h)}$ but not on its sign. It is usually described either by the Marcus expression

$$\gamma_{ij} = |t_{ij}^{(e,h)}|^2 \sqrt{\frac{\pi}{\hbar^2 T \varepsilon_\lambda}} \exp \left(-\frac{(\varepsilon_{ij}^{(e,h)})^2 + \varepsilon_\lambda^2}{4\varepsilon_\lambda T} \right), \quad (2)$$

or by the Miller-Abrahams expression

$$\gamma_{ij} = \gamma_0 |t_{ij}^{(e,h)}|^2 \exp \left(-\frac{|\varepsilon_{ij}^{(e,h)}|}{2T} \right). \quad (3)$$

Here ε_λ is the reorganization energy, $t_{ij}^{(e)}$ is the LUMO overlap integral for a pair of sites $i - j$, and $t_{ij}^{(h)}$ is the HOMO overlap integral. γ_0 is a phenomenological constant that controls electron-phonon interaction. Marcus rates rely on the conservation of vibrational modes during electron hopping, due to the atomic masses being much larger than the electron mass [25]. However, it is known that hops involving a large decrease in energy still occur with phonon emission, making

their rates more comparable to the Miller-Abrahams expression [22]. The effects of the two hopping rate expressions are analyzed in Appendix C. It appears that the specific type of rates (Miller-Abrahams or Marcus) is less significant for the phenomena discussed in this article compared to the overall relationship between hopping rates and spin-precession time. As a result, we primarily adopt the Miller-Abrahams rates for their simplicity.

Equations (1)–(3) stand for a hop to an unoccupied site. The hops to a site occupied by a charge carrier with the same type as the hopping carrier are prohibited due to the strong Coulomb repulsion. The hop to a site occupied by a carrier with a different type (for example a hole hop to a site occupied by an electron) leads to the formation of an exciton. The Coulomb attraction makes this process faster than a hop to a free orbital. It can be described by the constant γ_0 in Eq. (3) substituted by a larger constant γ_s or γ_t . Here γ_s corresponds to the electron and hole spins being in singlet states, and γ_t corresponds to a triplet state. The different rates of singlet and triplet exciton formation are required for the exciton OMAR mechanism [39]. In our model, the excitons themselves are not considered. Therefore, when both an electron and a hole appear on a site, it becomes unoccupied within our simulation. It is a valid simplification when the average site occupation number is small.

The boundary conditions along the y axis are periodic. The numerical samples have boundaries in the x direction that stand for electron and hole injection from the contacts. The boundary at $x = 0$ describes the electron contact. On each unoccupied site i of the contact, the electron can appear with the rate $g_i^{(e)}$. If a hole reaches a site of the electron contact, it recombines with electrons in the contact and is removed from the simulation. The second boundary describes the hole contact where holes can appear with the rates $g_i^{(h)}$. If an electron hops on a hole contact site, it is also removed from the simulation.

The transport can be described by the spin-independent Monte Carlo algorithm when the singlet and triplet exciton formation rates are the same. In this case, spin correlations do not appear and a magnetic field does not affect transport. However, it is a good starting point for the description of our algorithm. It starts with electrons and holes randomly distributed over sites of the lattice. The conventional kinetic Monte Carlo algorithm presumes that on each step s of the algorithm, the set of possible processes should be considered [45]. In our case, they include electron and hole hops (that do or do not lead to exciton formation) and the charge carrier generation at the contacts. On each step the process p occurs with the probability

$$P_p = \frac{r_p}{\rho_s}, \quad \rho_s = \sum_{p=1}^{\mathcal{N}} r_p. \quad (4)$$

Here r_p is the rate of process p , and ρ_s is the total rate of all the processes possible on step s . The step corresponds to the time interval $\tau(s)$ that is randomly selected with distribution density

$$\mathcal{F}(\tau) = \rho_s e^{-\rho_s \tau}. \quad (5)$$

However, we make a modification to this conventional scheme that would be required to merge the discrete kinetic Monte Carlo algorithm and continuous spin precession. Instead of the processes themselves, we consider the attempts of the processes. If site i is occupied by an electron, the attempt of its hop from site i to site j is included into the algorithm without considering the occupation of site j . The rate r_p of this attempt is equal to

$$r_p = \frac{\gamma_{\text{exc}}}{\gamma_0} r_{ij}^{(e)}, \quad \gamma_{\text{exc}} = \gamma_s + \gamma_t. \quad (6)$$

Similarly, if site i is occupied with a hole, the attempt of its hop to site j is added to the algorithm without considering the occupation of site j and with the rate $\gamma_{\text{exc}} r_{ij}^{(h)} / \gamma_0$.

When an attempt to hop from site i to site j is selected at some Monte Carlo step s , the hop itself is accepted only with a certain probability. This probability depends on the occupation of the destination site. If the site j is unoccupied, the hop is made with the probability $\gamma_0 / \gamma_{\text{exc}}$. If the hop leads to exciton formation, it is accepted with the probability $(p_s \gamma_s + p_t \gamma_t) / \gamma_{\text{exc}}$, where p_s is the probability of electron and hole spins to be in a singlet state, and $p_t = 1 - p_s$ is their probability to be in a triplet state. When the spins are not correlated, $p_s = 1/4$. A hop leading to the double occupation of a site with charge carriers of the same type is never accepted. If the selected hop is rejected on Monte Carlo step s , the step $s + 1$ starts from the same state of the system as the previous one.

Such a modification of the algorithm does not change its results, and in some cases it increases its efficiency [46]. In our case, it allows a simple generalization of the algorithm to include the spin correlations and $\gamma_s \neq \gamma_t$ because such an algorithm does not require knowledge of spin correlations at the process selection stage.

III. SPIN CORRELATIONS

In this section, we show how the spin correlations can be added to our algorithm. Only pair correlations between electron and hole spins are considered in this article. They are defined as the averaged products $\overline{s_i^\alpha s_j^\beta}$ of the spin projections s_i^α and s_j^β of spins i and j to the Cartesian axes α and β , respectively.

The correlations are conserved in the hopping process; however, between the hops they are modified due to the spin precession according to the master equation

$$\frac{d}{dt} \overline{s_i^\alpha s_j^\beta} = \epsilon_{\alpha\gamma\alpha'} \Omega_i^\gamma \overline{s_i^{\alpha'} s_j^\beta} + \epsilon_{\beta\gamma\beta'} \Omega_j^\gamma \overline{s_i^\alpha s_j^{\beta'}}. \quad (7)$$

Here $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol. Ω_i^γ is the projection of the spin-precession frequency $\mathbf{\Omega}_i$ on the site where electron or hole i is located on the axis γ . $\mathbf{\Omega}_i$ is equal to $\mathbf{\Omega}_i^{(e)}$ for an electron or to $\mathbf{\Omega}_i^{(h)}$ for a hole. When the carriers hop between empty molecular orbitals, the frequencies $\mathbf{\Omega}_i$ and $\mathbf{\Omega}_j$ are correspondingly updated. The summation over repeated indexes is assumed.

As long as only the hops from single occupied to unoccupied sites occur in the Monte Carlo algorithm between moments of time τ_1 and $\tau_2 > \tau_1$, the time evolution of the

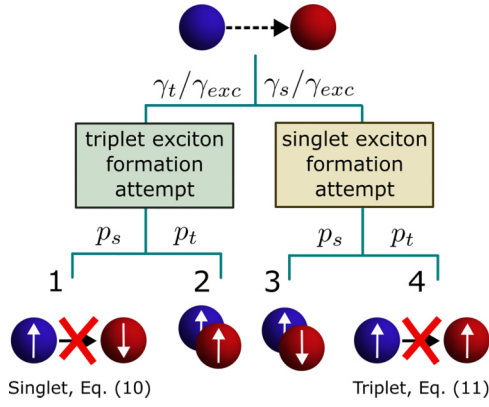


FIG. 2. The diagram of the choices made in the algorithm when the exciton formation process is selected and the four possible outcomes in the simulation. 1. The process is rejected, Eq. (10) is applied to the spin correlation to take into account that spins are in a singlet state. 2. The triplet exciton is formed. 3. The singlet exciton is formed. 4. The process is rejected, Eq. (11) is applied to the spin correlation to take into account that the spins are in a triplet state.

correlation can be expressed as follows:

$$\overline{s_i^\alpha s_j^\beta}(\tau_2) = R_{\alpha\alpha'}^{(i)}(\tau_2, \tau_1) R_{\beta\beta'}^{(j)}(\tau_2, \tau_1) \overline{s_i^{\alpha'} s_j^{\beta'}}(\tau_1). \quad (8)$$

Here $R_{\alpha\alpha'}^{(i)}(\tau_2, \tau_1)$ is the matrix that describes the total rotation of spin i between times τ_1 and τ_2 . $R_{\beta\beta'}^{(j)}(\tau_2, \tau_1)$ is a similar matrix for the spin j . The summation over repeated indices is assumed. Note that the spin i can be correlated with several other spins; however, the matrix $R_{\alpha\alpha'}^{(i)}(\tau_2, \tau_1)$ is the same for all these correlations.

The possibilities to hop from a site i occupied by an electron to a site j occupied by a hole (and vice versa) are included into the Monte Carlo algorithm. It is the part of the algorithm where the correlations play an important role. If such a possibility is selected at a particular step, several choices are made that are schematically shown in Fig. 2. The algorithm initially identifies which of the two processes is attempted. It is the formation of a singlet exciton with a probability of $\gamma_s/\gamma_{\max}$ and the formation of a triplet exciton with a probability of $\gamma_t/\gamma_{\max}$. Following this, the algorithm identified the spin state of an electron and a hole. They are in the spin singlet state with a probability

$$p_s = \frac{1}{4} - \sum_{\alpha} \overline{s_i^\alpha s_j^\alpha}. \quad (9)$$

Their state is a triplet with a probability $p_t = 1 - p_s$.

When the spin state aligns with the selected process (e.g., attempting singlet exciton formation with electron and hole spins in the singlet state), exciton formation takes place. In our model, excitons are subsequently removed from the simulation after their creation. Any correlations involving spins i and j are also removed. In the other case, the exciton formation fails and the electron and hole remain at their respective sites. Yet, the correlation between spins i and j should be adjusted to reflect the determined state of spins i and j . This stage in the algorithm marks the initial appearance of correlations.

If the triplet exciton formation fails and the spin state of the electron and hole is a singlet, the correlation between spins i

and j appears to be

$$\overline{s_i^\alpha s_j^{\beta'}} = -\frac{1}{4} \delta_{\alpha\beta}. \quad (10)$$

Here a “prime” in $\overline{s_i^\alpha s_j^{\beta'}}$ means that we consider the correlation immediately after the failed attempt of exciton formation. If the two spins form a singlet state, they are never correlated with other spins, therefore the correlations of spins i and j with other electrons and holes are eliminated.

If the singlet exciton formation fails because spins i and j are in a triplet state, the situation is somewhat more complex. There are three triplet quantum states, and the apparent correlation depends on the initial state of spins i and j . The expression for the correlation in this case is derived in Appendix A,

$$\overline{s_i^\alpha s_j^{\beta'}} = \frac{\overline{s_i^\alpha s_j^\beta} + \overline{s_i^\beta s_j^\alpha}}{2p_t} + \frac{1}{4p_t} \left(\frac{1}{4} - \overline{s_i^\gamma s_j^\gamma} \right) \delta_{\alpha\beta}. \quad (11)$$

Here $\overline{s_i^{(\alpha)} s_j^{(\beta)'}}$ is the spin correlation after the failed singlet exciton formation attempt, and $\overline{s_i^{(\alpha)} s_j^{(\beta)}}$ is the correlation before the attempt.

IV. INTERMEDIATE AVERAGING OVER HOPPING TIMES

The approach for incorporating spin correlations into the Monte Carlo algorithm outlined in Sec. III exhibits a notable drawback. Once established, correlations persist without relaxation during the hops of electrons and holes from single-occupied sites to unoccupied ones. In actual systems, spin relaxation takes place due to the interplay of spin precession and the random timing of hops. The averaged rotation matrix $R_{\alpha\beta}^{(i)}(\tau_2, \tau_1)$ tends to zero when a large number of hops occur between times τ_1 and τ_2 . However, in the conventional Monte Carlo algorithm, the times of hops are well-defined and $R_{\alpha\beta}^{(i)}(\tau_2, \tau_1)$ always remains an orthogonal matrix. Achieving spin relaxation requires averaging over many runs of the Monte Carlo algorithm. It is desirable, however, to include spin relaxation into a single run.

Any quantity A in a Monte Carlo simulation is calculated as an average over “Monte Carlo paths,” i.e., the hop attempts and their times,

$$\langle A \rangle = \sum_w p_w A(w). \quad (12)$$

Here p_w is the probability of the path w . It is the product of all the probabilities of process attempts in this path,

$$p_w = \prod_n p_{w,n}, \quad p_{w,n} = \exp(-\rho_n t_n) r_n dt_n, \quad (13)$$

where r_n is the rate of the n th hop of the path, t_n is the time between hops n and $n-1$, and ρ_n is the total rate of all the process attempts possible after the hop $n-1$.

When the system can be divided into two independent parts, the probability of any path can be decoupled,

$$p_w = p_{w_1} p_{w_2}. \quad (14)$$

Here p_{w_1} is the probability of the path in the first subsystem, and p_{w_2} is the same for the second subsystem.

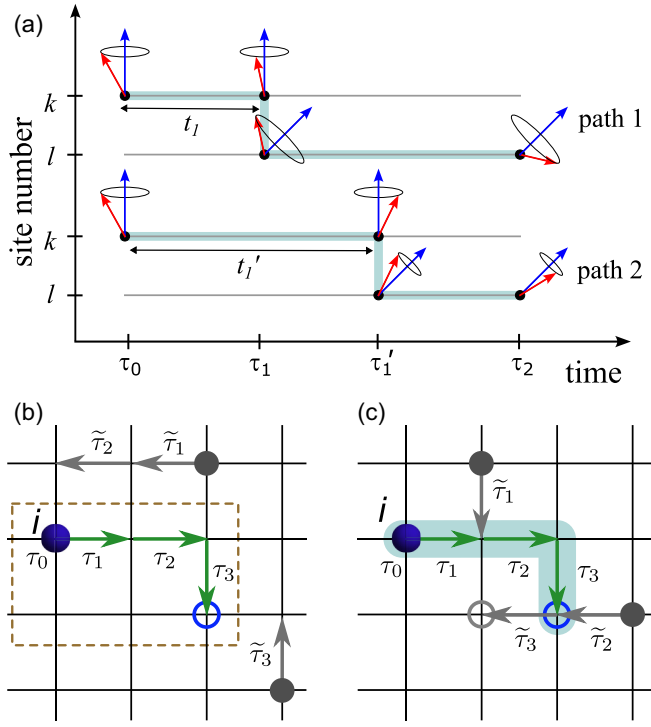


FIG. 3. (a) The spin rotation on the Monte Carlo paths that include a single hop between sites k and l made at arbitrary time τ_1 , $\tau_0 < \tau_1 < \tau_2$. (b), (c) The conditions of the independence of electron i hops from other electrons and holes. (b) Hops of the electron at times τ_1 – τ_3 are independent from the other hops at times $\tilde{\tau}_1$ – $\tilde{\tau}_3$. (c) The scenarios when the independence is broken: electron i hops (at the time τ_3) to a site that was occupied since τ_0 ; the other charge carrier hops (at the time $\tilde{\tau}_1$) to a site that was visited by electron i since τ_0 .

Let us consider the first subsystem to be related to the i th electron (or hole) and the second one to all other charge carriers. The conditions for these subsystems to be independent are discussed below. We are interested in the averaging of spin correlations over a set of paths where the i th electron makes identical hops 1, 2, ..., N but with the arbitrary waiting times $t_1, t_2, \dots, t_N$. The spin rotations at these paths are different, as illustrated in Fig. 3(a) for a specific case of one hop between sites k and l made at an arbitrary moment of time τ_1 in the interval (τ_0, τ_2) . We consider the initial time τ_0 of the path and its final time $\tau_N = \tau_0 + \sum_{n=1}^N t_n$ always to be the same. The rotation matrix $\langle \hat{R} \rangle$ averaged over these paths equals

$$\langle \hat{R} \rangle = \frac{\int dt_1 \dots dt_N \hat{R}_N(t_N) \dots \hat{R}_1(t_1) e^{-\rho_1 t_1} \dots e^{-\rho_N t_N}}{\int dt_1 \dots dt_N e^{-\rho_1 t_1} \dots e^{-\rho_N t_N}}. \quad (15)$$

Here $\hat{R}_n(t_n)$ is the rotation matrix corresponding to the spin precession at the n th step of the path for the time t_n . It is possible to calculate $\langle \hat{R} \rangle$ analytically; however, the resulting expression is quite cumbersome and is provided in Appendix B.

The averaged rotation matrix calculated with Eq. (15) incorporates at least some part of the spin relaxation and tends to zero at large times. As long as the i th electron is separated from all other charge carriers [see Fig. 3(b)], $\langle \hat{R} \rangle$ can

be included into the Monte Carlo algorithm instead of the normal rotation matrix $R_{\alpha\beta}^{(i)}(\tau_0, \tau_N)$, which is the main idea of this section. It represents the analytical averaging of results over the described subset of Monte Carlo paths and keeps the algorithm correct. However, it can only be done when the outcomes (acceptance probabilities) of all the hop attempts in the simulation are the same for all the values $t_1, \dots, t_N$ in Eq. (15).

According to these arguments, we introduce the following procedure of the intermediate averaging. For all electrons and holes involved in spin correlations, we keep in mind their spin rotation matrices and times τ_0 when these matrices were computed. When an electron or hole i hops, we monitor its independence from the rest of the system. As long as it persists, we only record the set of sites visited by the carrier since τ_0 . Independence is compromised in the two scenarios. First, the carrier i may hop to a site that was previously occupied at some point of time since τ_0 . In this case, the actual hopping time becomes crucial, as the result of the hop depends on the current status of the site. Second, a site previously visited by electron i may become occupied by another electron or hole at some point after τ_0 . The possibility of such an occupation depends on the actual position of electron i and thus on its hopping times. These two situations are illustrated in Fig. 3(b).

Upon encountering either of these conditions, we calculate the rotation matrix with Eq. (B7) from Appendix B and start tracking the independence again. When a spin correlation is important for exciton formation, the rotation matrices for the participating electron and hole should also be calculated.

V. RESULTS OF THE SIMULATION

In this section, we present the results of KMC simulations for various model systems. We start the discussion with the results for the 6×6 numerical samples similar to the one shown in Fig. 1. Both LUMO and HOMO energies on all the molecules have a Gaussian density of states (GDOS) with the width $\delta\epsilon$. The typical width of this distribution in organic semiconductors varies from ~ 0.02 eV in highly conductive materials like BTBT [47] to ~ 0.1 eV in the less conductive ones [48]. For the first simulation, we select the value $\delta\epsilon = 2T$, which, for room temperature, corresponds to $\delta\epsilon = 0.05$ eV.

The overlap integrals $t_{ij}^{(e,h)}$ between the neighbors are considered to be significantly smaller than $\delta\epsilon$, leading to the hopping transport. We consider the Miller-Abrahams hopping rates described by Eq. (3) (the comparison between Marcus and Miller-Abrahams rates is made in Appendix C). The rates $\gamma_0 |t_{ij}|^2$ for neighbor pairs of molecules are randomly selected within the interval $(0, W_h \Delta)$, where W_h is a constant controlling the overall relation between hopping rates and spin-precession frequencies, and $2\pi/\Delta \sim 5$ ns corresponds to a spin precession period in the 10 mT magnetic field. Note that the typical hop waiting times are slower than this value due to the energy disorder, which agrees with the results of *ab initio* simulations for Alq3 [22]. The typical values for the physical quantities important for this simulation are collected in the table on Fig. 4.

$\delta\varepsilon$	width of GDOS	50 meV
T	temperature	25 meV
$\hbar\Delta$	hyperfine interaction	10^{-6} eV
B_Δ	Overhauser field	10 mT
$2\pi/\Delta$	spin precession period	5 ns

FIG. 4. Table of the scales for energies, magnetic fields, and times relevant for the simulation.

The electron and hole generation rates $g_i^{(e)}$ and $g_i^{(h)}$ at the corresponding contacts are selected in the interval $(0, W_g W_h \Delta)$, where the constant W_g controls the ratio between hopping and generation times. We consider $W_g \leq 10^3$, which corresponds to relatively small concentrations of electrons and holes, and our samples being in the diffusion transport regime. The exciton formation rates are $\gamma_s = 40\gamma_0$ and $\gamma_t = 6\gamma_0$. It shows that both singlet and triplet exciton formation is more efficient than ordinary hops due to the Coulomb attraction between electrons and holes; however, singlet excitons form significantly faster than triplet ones.

For each numerical sample, our calculations were conducted until 3×10^6 hops are made. We calculated the number of all the electrons N_e and holes N_h that pass through the system and the numbers of singlet N_s and triplet N_t excitons formed during the simulation. We were interested in the current $j = e(N_e + N_h)/t_{\text{sim}}$, where t_{sim} is the simulation time, and the quantum efficiency $q = 2N_s/(N_e + N_h)$ of electroluminescence. In the definition of q , we assumed that only singlet excitons recombine radiatively and, therefore, contribute to the luminescence. All the results are averaged over 100 disordered numerical samples unless noted otherwise.

In Fig. 5, we show the dependence of magnetoconductivity and quantum efficiency on the parameter W_g , and we compare it with the Lorentzian curve:

$$\frac{\delta j}{j(0)}, \frac{\delta q}{q(0)} = -A \frac{B^2}{B^2 + B_0^2}. \quad (16)$$

Here $\delta j = j(B) - j(0)$ and $\delta q = q(B) - q(0)$. A is the Lorentzian amplitude, and B_0 is its width. We set $W_h = 1$ so that the fastest possible hopping rates are comparable to the frequencies of spin precession. Magnetic field is given in units of the typical Overhauser field $B_\Delta = \Delta/\mu_B g \sim 10$ mT.

Figure 5(a) shows that both magnetoconductivity and the effect of magnetic field on luminescence can be described by the Lorentzian dependence with a similar width B_0 . However, the magnetoconductivity has a much smaller amplitude. Figures 5(b) and 5(c) show the widths B_0 and the amplitudes A of magnetoconductivity and the quantum efficiency as a function of generation rate W_g . The width and the amplitude for the quantum efficiency are not significantly modified due to different generation rates. However, the magnetoconductivity amplitude decreases with decreasing W_g because at small

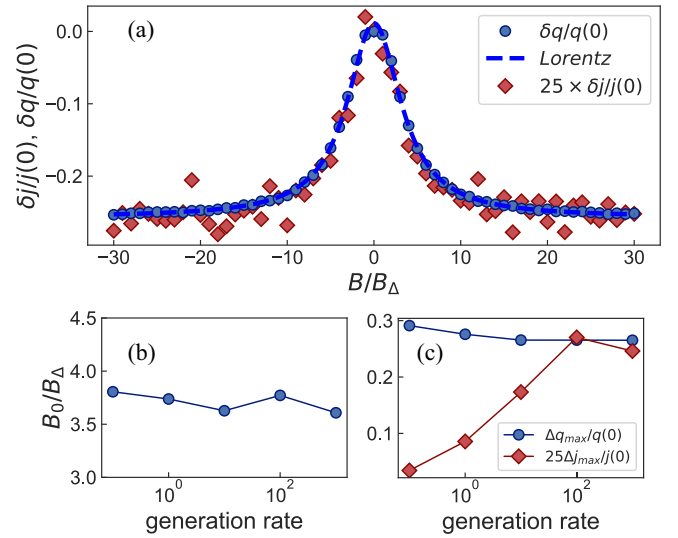


FIG. 5. The results of the simulation for different generation rates W_g . (a) The comparison between the shapes of dependencies $\delta q/q(0)$ and $\delta j/j(0)$ with Lorentzian. The calculations are made for $W_g = 10^2$ and averaged over 300 disorder realizations. (b) The dependence of the width B_0 on the generation rate. (c) The amplitudes A for $\delta q(B)/q(0)$ and $\delta j(B)/j(0)$ dependencies as functions of W_g .

generation rates most of the electrons and holes reach the opposite contact without recombination with each other. In the following part of the article, we focus on the quantum efficiency q .

In Fig. 6, we study the dependence $q(B)$ for different hopping rates W_h and $W_g = 1$. Figure 6 shows that this dependence can always be described as a Lorentzian. It is not sensitive to W_h as long as the hops stay slow compared to the spin precession, in agreement with [35]. However, when the hopping is allowed to be faster than the precession ($W_h > 1$), the situation changes. The dependence $q(B)$ significantly broadens (from $B_0 \approx 3.6B_\Delta$ to $B_0 \approx 4.8B_\Delta$) and its amplitude decreases with W_h . At a very fast hopping rate, correlated electrons and holes are separated too quickly for their spin dynamics to affect the exciton formation process. We believe that the regime with elevated B_0 but a relatively large amplitude of $\delta q(B)$ dependence is related to the scenario in which only selected hops occur faster than spin precession, while the majority of hops remain slow due to the energy disorder.

To explore this scenario, we constructed numerical samples consisting of $N \times M$ clusters with different kinds of molecules. One type of molecule can be easily occupied by an electron but is only rarely visited by the hole because of its large HOMO energy. The other kind has HOMO energy that allows easy occupation by a hole, but a high LUMO energy prevents its occupation by an electron. This scenario may correspond to spatially correlated energetic disorder associated with the electric dipole moments of organic molecules [49–52] or to the material being composed from donor and acceptor molecules [53]. The hopping rate W_h was selected equal to 125 and random energy disorder equal to 0.17, making the hops inside clusters much faster than spin precession. However, the energy of the clusters was either increased or decreased by $3.5T$ due to the electric potential. The HOMO

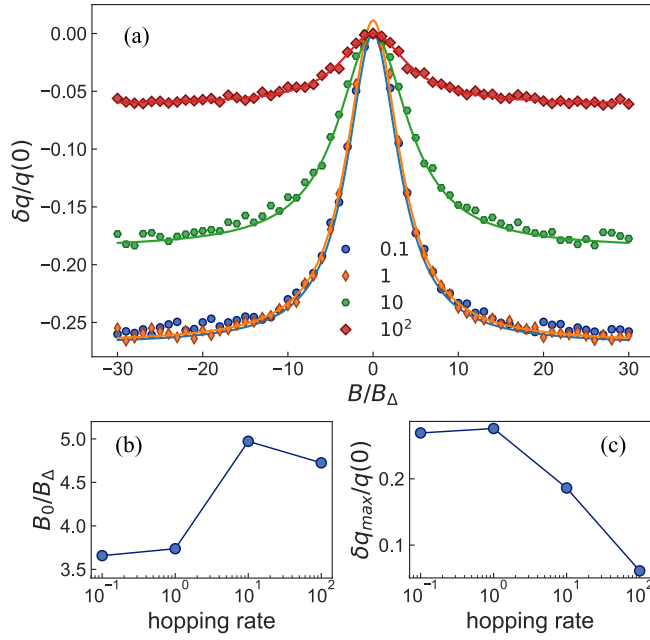


FIG. 6. The results of the simulation for different hopping rates W_h and $W_g = 1$. (a) The comparison between the dependencies $\delta q/q(0)$ for the different values of W_h , as shown in the legend, and Lorentzian shape. (b) The dependence of the width B_0 over hopping rate W_g . (c) The dependence of the amplitude A over hopping rate W_g .

energies were changed in the opposite direction compared to the LUMO energies (when the electron energy was increased, the hole energy was decreased). Figure 7(a) shows the electron energies $\varepsilon_i^{(e)}$ (marked with colors) and tunneling amplitudes γ_{ij} (as linewidths) for a sample with 2×2 clusters. Besides the “islands” themselves, the sample contains contact sites with energies close to zero. The electrons and holes are injected into the corresponding clusters as shown with blue (for electrons) and red (for holes) arrows in Fig. 7(a). When the electrons and holes reach the opposite side of the sample, they are removed from the simulation as in the previous calculations. The strong Coulomb energy prevents electrons from hopping into a hole cluster and *vice versa*, however the barrier can be overcome during the exciton formation due to the large values $\gamma_s = 40$ and $\gamma_t = 6$. It makes the singlet exciton formation slightly faster than spin precession in an Overhauser field and triplet exciton formation slightly slower than this preces-

sion. For each of the considered cluster sizes, the averaging over 100 disorder realizations was made, although the effect of the disorder is weak in these samples. For each of these numerical samples, we conducted the calculations until 10^8 hops were made.

In Figs. 7(b) and 7(c), we describe the dependence $[q(B) - q(0)]/q(0)$ of quantum efficiency on the magnetic field in such cluster samples. Figure 7(b) shows that the shapes of the dependencies $q(B)$ for different cluster sizes, rescaled over both axes, can be described by the same curve close to the Lorentzian. In Fig. 7(c), we compare the widths B_0 and amplitudes A of the dependencies. In all the cases, the value of B_0 is larger than $3.6B_\Delta$ corresponding to results shown in Fig. 5. For the 1×2 clusters, $B_0 = 5.6B_\Delta$ is close to the largest values obtained for the quasiuniform numerical samples (Fig. 6). For 1×3 and 2×2 clusters, the dependencies are even wider. The amplitudes A of $[q(B) - q(0)]/q(0)$ for 1×2 and 1×3 clusters are quite high (~ 0.1), while for 2×2 clusters the amplitude is somewhat reduced ($A = 0.05$).

VI. DISCUSSION

Our results show that when some of the hops are faster than spin precession, the shape of the electroluminescence dependence on the magnetic field is influenced not only by the strength of the hyperfine interaction itself, but also by the distribution of hopping rates. In particular, when the majority of hops are slow, but small clusters exist with the hops much faster than spin precession, the width of the dependence can significantly increase without a strong impact on its amplitude.

The Monte Carlo algorithm discussed in this article is tailored to studying the quantum efficiency of OLEDs and their dependence on the magnetic field. Therefore, we focus on the spin relaxation due to the hyperfine interaction with the nuclear spins, which is known to be one of the most important spin relaxation mechanisms in organic semiconductors, and it can be easily affected by the magnetic field. The second important spin relaxation mechanism is probably the spin-orbit interaction [54]. It leads to a spin rotation during the hop. In terms of our algorithm, it would correspond to the multiplication of matrix $R_{\alpha\alpha'}^{(i)}$ to some transformation matrix describing this rotation at the moment of hop. Although it is not a part of the current article, we believe that it still will be possible to make an intermediate averaging (similar to the one

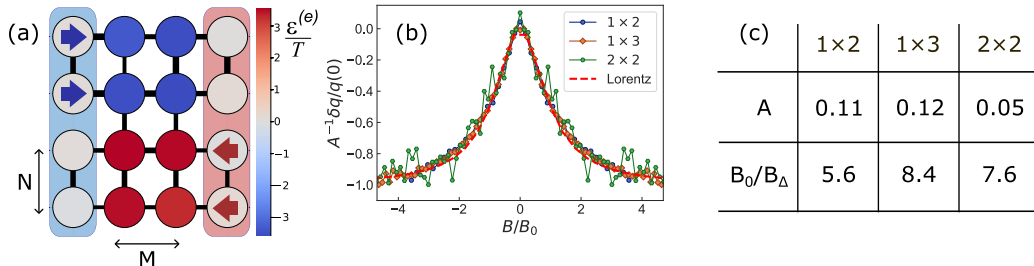


FIG. 7. The results of the simulation of “cluster” samples. (a) The structure of a sample with the cluster size $N = M = 2$. (b) Rescaled $\delta q(B)/q(0)$ dependencies for the samples with different cluster sizes shown in the legend compared to the Lorentzian. (c) The amplitudes and widths of the dependencies for the different cluster sizes.

described in Sec. IV and Appendix B) in this case. The third relaxation mechanism, the spin-phonon interaction, does not require hops. It can be introduced into the spin dynamics as an additional term $-s_i^\alpha s_j^\beta / \tau_{s-ph}$ on the right-hand side of Eq. (7), where τ_{s-ph} is the typical time of spin-phonon interaction. However, we believe this mechanism to be the least important of the three: it is known that corresponding times in molecules can reach ~ 1 ms [55], which is too large compared to the other mechanisms.

The current algorithm is designed for disordered organic semiconductors with low mobility, which can be described using the small polaron theory. The organic semiconductors with higher mobility $\mu \gtrsim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are typically characterized by the transient localization regime. In this regime, charge transport arises from a complex interplay between electronic and nuclear dynamics [56], which significantly influences spin relaxation [57]. Theoretical approaches to this regime are still under development, and they include the combined treatment of classical nuclear dynamics and quantum electron transport [56,58] and the use of matrix product states in one-dimensional systems [59]. One potential approach is a generalized KMC method that integrates Monte Carlo steps with numerical diagonalization of small portions of the one-electron Hamiltonian performed after each step [60]. However, while it might be possible to adapt our algorithm to such methods, this would require substantial modifications.

The influence of magnetic fields on OLED electroluminescence is a promising phenomenon with applications in magnetic sensors [15,61]. However, the effective use of these sensors requires miniaturization, which, in turn, demands a deeper understanding of the microscopic spin properties in organic semiconductors. Recent experimental studies have revealed unexpected variations in the hyperfine interaction strength, as measured by the width of the magnetoluminescence curve (corresponding to B_0 in our notation). These variations can be as large as 27% across a series of identical devices [61], and the measured hyperfine interaction strength exhibited slow time dynamics on the timescale of minutes [62]. Such fluctuations are critical for device performance and could limit their sensitivity. The results obtained within the toy models in Sec. V suggest that these variations are not due to changes in the hyperfine interaction itself (which is a molecular property and generally stable) but are instead related to disorder in the hopping times, which is important for transport in amorphous organic semiconductors [63,64]. To reliably assess the contribution of hopping rate disorder to the apparent distribution of hyperfine interaction strengths, however, a multiscale modeling approach is needed. This would combine the current algorithm with molecular dynamics and *ab initio* studies.

Beyond magnetoelectroluminescence, our algorithm, with some modifications, can describe a broad range of phenomena where spin correlations play a crucial role. For instance, the bipolaron mechanism of OMAR [35] requires us to consider the possibility of a single molecule being occupied by two electrons or two holes. If spin polarizations were added to the algorithm together with exchange interaction, it would allow us to study the spin relaxation and dynamic spin polarization. Probably the most complex would be the introduction to our

algorithm of the long-range particle-particle interactions such as the Coulomb interaction or the long-range magnetic dipole interaction between distant spins [65]. While these interactions are compatible with the KMC method itself, they would interfere with the intermediate averaging procedure.

While the Monte Carlo simulations may be less memory-intensive compared to correlation master equation methods, especially when spin correlations at large distances are important, they are more time-consuming. This is particularly true when the distribution of the hopping rates in the material is very broad, necessitating a significant number of “fast” hops to be made before the simulation adequately includes a reasonable number of “slow” hops. Therefore, the choice of the optimal method should be based on the specific problem.

In conclusion, we have developed a kinetic Monte Carlo algorithm capable of incorporating spin correlations into simulations without the requirement that electron hops are much slower than spin precession in the Overhauser field of nuclear spins. We demonstrate that even a small portion of hopping rates faster than this precession can significantly modify the measured width of the OLED quantum efficiency dependence on the magnetic field.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF EQ. (11)

To derive the expression for correlations after a failed singlet exciton formation attempt, we explicitly write the density matrix of spins i and j in the state described by correlation $s_i^{(\alpha)} s_j^{(\beta)}$,

$$\rho(i, j) = \left(\sum_{x_1, x_2} \overline{s_i^{x_1} s_j^{x_2}} \sigma_i^{x_1} \otimes \sigma_j^{x_2} \right). \quad (\text{A1})$$

Here, x_1 and x_2 can be equal to either 0 or Cartesian coordinates x , y , or z . $s_{i,j}^{(0)}$ equals $1/2$; σ^x , σ^y , and σ^z are Pauli matrices; and σ^0 is 2×2 unit matrix.

The transformation of $\rho(i, j)$ when the spins i and j are found to be in a triplet state can be expressed as follows:

$$\rho(i, j) \rightarrow \frac{1}{p_t} \Pi_t \rho(i, j). \quad (\text{A2})$$

Here $\hat{\Pi}_t$ is the linear operator of projection of the density matrix on the subspace of triplet states. It can be expressed as a product of three operators,

$$\Pi_t = \Pi^{(\rightarrow)} \Pi_t^{(0)} \hat{\Pi}^{(\leftarrow)}. \quad (\text{A3})$$

Here $\Pi^{(\leftarrow)}$ describes the transformation of the density matrix from the “spin basis” ($\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\downarrow$) to the “singlet-triplet” basis, where the states are enumerated as “singlet,” “triplet +,” “triplet 0,” and “triplet −.” $\Pi^{(\leftarrow)} \rho(i, j) = \hat{T} \rho(i, j) \hat{T}^T$, where

$\hat{T}$ is the unitary matrix of this transformation,

$$\hat{T} = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (\text{A4})$$

$\Pi_t^{(0)}$ is the projection operator in a singlet-triplet basis. It corresponds to the multiplication of $\rho(i, j)$ by the matrix

$$\Pi_t^{(0)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (\text{A5})$$

The operator $\Pi^{(\rightarrow)}\rho = \hat{T}^T \rho \hat{T}$ describes the backward transition from the singlet-triplet basis to the initial basis.

Because Π_t is a linear operator, it is enough to calculate its action on the basis matrix to derive the result of its action on an arbitrary matrix,

$$\Pi_t(\sigma^0 \otimes \sigma^0) = \frac{3}{4}\sigma^0 \otimes \sigma^0 + \frac{1}{4}\sigma^\alpha \otimes \sigma^\alpha, \quad (\text{A6})$$

$$\Pi_t(\sigma^0 \otimes \sigma^\alpha) = \hat{\Pi}_{t,ij}(\sigma^\alpha \otimes \sigma^0) = \frac{\sigma^0 \otimes \sigma^\alpha + \sigma^\alpha \otimes \sigma^0}{2}, \quad (\text{A7})$$

$$\begin{aligned} \Pi_t(\sigma^\alpha \otimes \sigma^\beta) &= \frac{\sigma^\alpha \otimes \sigma^\beta + \sigma^\beta \otimes \sigma^\alpha}{2} \\ &+ \frac{\delta_{\alpha\beta}}{4}(\sigma^0 \otimes \sigma^0 - \sigma^\gamma \otimes \sigma^\gamma). \end{aligned} \quad (\text{A8})$$

By combining Eq. (A2) with Eqs. (A6)–(A8), we derive the expression for the correlations after the failed singlet exciton formation attempt.

APPENDIX B: ANALYTICAL EXPRESSION FOR $\bar{R}$

The dependence of the rotation matrix $\hat{R}_i(t_i)$ on the precession frequency Ω_i and time t_i can be expressed as follows:

$$\hat{R}_i(t_i) = \hat{1} + \sin(\Omega_i t_i) \hat{O}_i + (1 - \cos(\Omega_i t_i)) \hat{O}_i^2, \quad (\text{B1})$$

where $\Omega_i = |\Omega_i|$ and

$$\hat{O}_i = \frac{1}{\Omega_i} \begin{pmatrix} 0 & \Omega_i^z & -\Omega_i^y \\ -\Omega_i^z & 0 & \Omega_i^x \\ \Omega_i^y & -\Omega_i^x & 0 \end{pmatrix}. \quad (\text{B2})$$

It is useful to modify this expression by expanding the sine and cosine functions into exponents, which leads to

$$\hat{R}_i(t_i) = \sum_{m=-1,0,1} \exp(im\Omega_i t_i) \hat{\Theta}_i^{(m)}, \quad (\text{B3})$$

where

$$\begin{aligned} \hat{\Theta}_i^{(0)} &= \hat{1} + \hat{O}_i^2, \quad \hat{\Theta}_i^{(-1)} = -\frac{\hat{O}_i^2 - i\hat{O}_i}{2}, \\ \hat{\Theta}_i^{(1)} &= -\frac{\hat{O}_i^2 + i\hat{O}_i}{2}. \end{aligned} \quad (\text{B4})$$

To treat Eq. (15), we introduce the function $f(x_1, \dots, x_N; t)$ of several rates $x_1, \dots, x_N$,

$$f(x_1, \dots, x_N; t) = \int e^{-x_1 t_1} \dots e^{-x_N t_N} \delta\left(t - \sum t_i\right) dt_1 \dots dt_N = \sum_{k=1}^N e^{-x_k t} \prod_{l=1}^N \frac{1}{x_l - x_k}. \quad (\text{B5})$$

Here the term $l = k$ is excluded from the product $\prod'$.

It allows us to make the integration in Eq. (15) analytically,

$$\langle \hat{R} \rangle = \frac{\sum_{m_1 \dots m_N} \hat{\Theta}_N^{(m_N)} \dots \hat{\Theta}_1^{(m_1)} f(\rho_1 - im_1 \Omega_1, \dots, \rho_N - im_N \Omega_N; \tau_N - \tau_0)}{f(\rho_1, \dots, \rho_N; \tau_N - \tau_0)}, \quad (\text{B6})$$

where the numbers $m_1, \dots, m_N$ can be equal either to 0 or ± 1 in agreement with Eq. (B3).

With some algebra, one can reduce the number of summations in Eq. (B6) and derive the following expression for $\langle \hat{R} \rangle$ that was used in our numerical calculations:

$$\begin{aligned} \langle \hat{R} \rangle &= \frac{1}{f(\rho_1, \dots, \rho_N; \tau_N - \tau_0)} \sum_{k=1}^N \sum_{m=-1}^1 \exp(-\rho_k(\tau_N - \tau_0) + im\Omega_k(\tau_N - \tau_0)) \\ &\hat{\Theta}_N(\rho_k - im\Omega_k) \dots \hat{\Theta}_{k+1}(\rho_k - im\Omega_k) \hat{\Theta}_k^{(m)} \hat{\Theta}_{k-1}(\rho_k - im\Omega_k) \hat{\Theta}_1(\rho_k - im\Omega_k), \end{aligned} \quad (\text{B7})$$

where we introduced

$$\hat{\Theta}_i(z) = \sum_{m=-1}^1 \frac{\hat{\Theta}_i^{(m)}}{\rho_i - im\Omega_i - z} = \frac{\hat{1} + \hat{O}_i^2}{\rho_i - z} + \frac{\hat{O}_i^2(\rho_i - z) - \hat{O}_i \Omega_i}{(\rho_i - z)^2 + \Omega_i^2}. \quad (\text{B8})$$

Equation (B7) contains only $3N(N-1)$ matrix multiplications in comparison to $3^N(N-1)$ multiplications required to compute the averaged rotation matrix with Eq. (B6). It makes Eq. (B7) applicable for the numeric simulations.

APPENDIX C: COMPARISON BETWEEN MILLER-ABRAHAMS AND MARCUS RATES

In this Appendix, we compare the simulation results using Miller-Abrahams and Marcus hopping rates, as described by

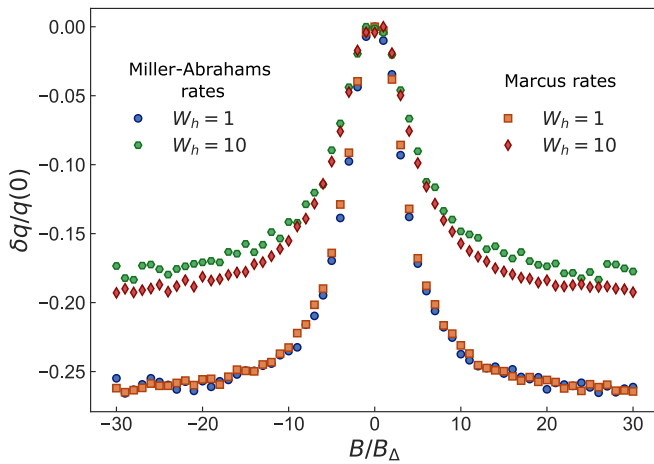


FIG. 8. Comparison between the OLED quantum efficiency calculated with Miller-Abrahams and Marcus hopping rates defined by Eq. (3) and Eq. (2), respectively, with W_h shown in the legend and the other parameters corresponding to the results presented in Fig. 6.

Eqs. (3) and (2), respectively, with the Miller-Abrahams rates corresponding to the results shown in Fig. 6. The parameters for Eq. (2) are chosen to ensure that the typical hopping rates in both cases remain comparable, although the rate

distributions differ due to the inherent differences between Eqs. (2) and (3).

To achieve this, we set the following parameters for the Marcus hopping rates to unoccupied sites: the overlap integrals $t_{ij}^{(e,h)}$ between neighboring sites are randomly selected so that $|t_{ij}^{(e,h)}|^2/\hbar T$ are uniformly distributed within the interval $(0, w_{\max})$, with $w_{\max} = 1.4W_h\Delta$. The reorganization energy, ε_λ , is set equal to the width of the molecular orbital energy distribution, i.e., $\varepsilon_\lambda = 2T$.

When electron or hole hopping leads to exciton formation, we adjust the hopping rate similarly to how it is modified for Miller-Abrahams hops. Specifically, we multiply the rate by γ_s/γ_0 for singlet exciton formation, and by γ_t/γ_0 for triplet exciton formation.

The simulation results are presented in Fig. 8. For $W_h = 1$, the results for the Miller-Abrahams and Marcus hopping rates are the same within computational precision. For $W_h = 10$, the Marcus hopping rates show a slightly stronger magnetic field effect on electroluminescence compared to the Miller-Abrahams rates. These results indicate that, at least for the parameters considered, the distribution of hopping rates has only a minor influence on magnetoelectroluminescence compared to the relationship between the typical hopping rates and the precession frequency.

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