MATERIALS AND ENERGY – Vol. 10

World Scientific Reference on

SPIN IN ORGANICS

Volume 3 – Magnetic Field Effects

Volume Editor: Markus Wohlgenannt

Editors

Zeev Valy Vardeny
University of Utah, USA

Markus Wohlgenannt
University of Iowa, USA

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CHAPTER 4

Room-Temperature Quantum Coherence in Emission from Organic Semiconductors

Nicholas J. Harmon∗ and Michael E. Flatté†

University of Iowa, USA
∗nicholas-harmon@uiowa.edu
†michael@flatte@mailaps.org

The role of quantum coherence in the excited states that produce light emission from organic semiconductors is reviewed. A general theoretical framework, applicable to emission from excitons as well as to emission from charge-transfer excitations/exciplexes is described. Analytic solutions exist for certain special cases, and numerical evaluation is possible for general situations. Connections to recent observations of very large room-temperature magnetoelectroluminescence in materials characterized by thermally-activated delayed fluorescence is discussed.

1. Introduction

Quantum coherence plays a central role in dynamical properties, with consequences for both the fundamental understanding of dynamics as well as for future quantum technologies.1,2 Although frequently the evolution of quantum coherence follows a simple path (such as in Fermi’s golden rule calculations of transition rates), whose simple form allows coherent effects to be neglected or trivialized, our focus here will be on the exceptions when coherent effects persist beyond the timescales for various other dynamical events and effects. Spin coherence forms a prominent subcategory within this area of quantum coherence,3,4 as spin coherence can persist to
room temperature and above, providing the mechanism for practical spin resonance sensing technologies, including magnetic resonance imaging. Spin resonance techniques are also applied to diagnose the origin of small numbers of trap states in electronic devices,\textsuperscript{5–8} relying on studies of the coherent response of various types of defects in an insulating barrier to radio-frequency electromagnetic waves. Spin manipulation and coherence also offer prospects for reducing the energy consumption of charge-based electrical devices\textsuperscript{9,10} through the manipulation of coherence times and spin filtering. There are even compelling proposals for biological implications of spin coherence in the dynamics of chemical reactions including as a technique to sense small magnetic fields by migrating birds.\textsuperscript{11,12} Connected through quantum coherence, a similar set of fundamental concepts and theories underlies the sensitivity of transport, luminescence, and chemical reactions, at room-temperature to extremely small magnetic fields, whose Zeeman energies are orders of magnitude smaller than the thermal energy.

Some general considerations motivate our focus on quantum coherence in the optical emission from organic semiconductors, caused by spin-spin interactions. The materials considered are nonmagnetic, so the interacting spins are in general randomly oriented and interact primarily in pairs. In order for such a pairwise interaction to influence phenomena at room temperature, the typical exchange and orbital energy scales associated with these spins have to be much larger than the thermal energy of $\sim 25$ meV, so a typical energy scale for exchange and orbital energies will be $\sim 1$ eV. In this Chapter substantial magnetic field effects (MFE’s) are found for very small external fields (i.e. $g\mu_B B \sim 1 \mu eV$, where $g$ is the Landé $g$ factor, $\mu_B$ is the Bohr magneton, and $B$ is the applied magnetic field). Thus the energies associated with these small external fields are much smaller than the exchange or orbital energy scales. This ordering of energy scales immediately focuses our attention on systems in an incoherent hopping transport regime. For external fields to switch off band transport, the energies associated with them would typically need to exceed the energy width of the band, which itself must be much larger than the thermal energy. Thus significant effects of small
external fields on band transport should not be expected, and the focus here is on systems exhibiting incoherent hopping transport. Many systems which have large exchange and orbital excitation energies, have incoherent hopping transport, and are thus sensitive to very small external fields at room temperature, are disordered organic and molecular materials. Other systems with similar behavior are localized states such as defects in an insulating barrier weakly coupled to their surroundings. Here we focus on disordered organic semiconductors. Although the emphasis here is on the phenomenon of luminescence, much of the analysis and theoretical dynamics can be applied to similar phenomena in conductivity and chemical reactions.

1.1. Optical excitation and luminescence in organic semiconductors

The field of photochemistry\textsuperscript{13} was established over two centuries ago with the Grotthuss-Draper law stating that light absorption may lead to chemical reactions. Photochemistry provides the microscopic understanding of many vital biological processes, including photosynthesis and vision. Chemical reactions that are not possible through thermal routes alone become allowed in photochemistry because the much larger optical energy provided (\(\sim eV\)) overcomes activation barriers that are inaccessible at practical temperatures (thermal energies <0.1 eV). As a result the typical considerations of equilibrium and detailed balance that apply to reactants and products in a thermally-activated chemical reaction may be modified by the near-instant departure of emitted light (luminescence) from the sample, leading to highly nonequilibrium reactions that are essentially not reversible.

Optical excitation in organic molecules is directly connected to spin statistics as the ground state of these organic molecules is a spin singlet and excitation by light typically preserves the spin quantum numbers of the excited material. Figure 1 compactly describes the basic nature of light-matter interactions in organic molecules. On the left, the ground state of a molecule is shown; two electrons occupy the highest occupied molecular orbital (HOMO). The Pauli exclusion principle requires their spins to orient antiparallel, which
is the singlet state denoted $S_0$. The wavy green line indicates light absorption, which kicks one electron to an excited state in the lowest unoccupied molecular orbital (LUMO). This excitation is named an exciton and is classified as an intra-molecular excitation — it exists on a single molecule (thus a Frenkel exciton, not a Wannier exciton). Absent a substantial spin-orbit interaction, the molecule does not respond to light with a preferential excitation of one spin direction over the other, and thus the excited spin orientation is random. This exciton can also be described as consisting of an electron and a hole; the “hole” indicates the absence of the electron in the HOMO. The hole has a positive charge and a spin whose orientation is opposite to that of the electronic state that has been emptied in the HOMO. As a result the effective spin of the hole is oriented parallel to that of the remaining electron residing in the HOMO. The positive charge of the hole in the HOMO keeps the excited electron in the LUMO attracted to its home molecule. If the excited electron is removed, leaving just a HOMO with a single electron (and thus one hole), the molecule is effectively positively charged, with the positive charge attributed to the hole.

The most likely electronic transition caused by optical absorption is an electric-dipole allowed transition, which does not flip the spin of the excited electron, and thus the exciton is usually generated in a singlet state, denoted $S_1$ for the first excited singlet state. The manifolds of excited singlet and triplet energies, along with the ground state, are illustrated in Fig. 2. The excited triplet state, $T_1$, commonly has a lower energy than the excited singlet state, due to
Room-Temperature Quantum Coherence in Emission

Fig. 2. (a) A schematic dependence of the energy of the first excited singlet ($S_1$) and triplet ($T_1$) exciton states, as a function of a general configuration coordinate. For nearby electron and hole the energy splitting is large, whereas for larger separations the energies approach each other. (b) Effective energy diagram of ground state ($S_0$) and singlet/triplet excited states. The shaded regions above each excited state energy denote combinations of the first excited exciton states with vibrations or variations of the configuration coordinate. $\Delta_{ST}$ is the energy gap or exchange splitting between the lowest-energy excited singlet and triplet states.

The exchange energy, $\Delta_{ST}$. Exchange is a many-body effect involving the many-electron state, and falls off exponentially with separation between the relevant carriers. Here the two involved carriers are the electron and hole, which are bound in an exciton. For excitons within small molecules the exchange energy often exceeds 1 eV. The electrons in these molecules are coupled to vibrations of the ions within the molecules, denoted phonons, which produces additional structure in Fig. 2. The thick edge shows the electronic energies when the molecules are in the vibrational ground state. The shaded region above denotes excited vibrational states combined with the same discrete electronic excitation, or excited many-body electronic excitations that are again combined with the same discrete electronic excitation. The excited vibrational states may also modify the electronic wave functions to a degree, and thus they can be referred to as vibronic states. From excitation into the $S_1$ band, even if the excitation energy does not correspond to the lowest-energy state in
the $S_1$ band, the emission emerges in largest yield from the lowest-energy $S_1$ state, which corresponds to no additional vibrational excitations (Kasha’s rule).\textsuperscript{14}

The low likelihood of generating $T_1$ excitons is a characteristic of the optical excitation process. Different forms of excitation, however, produce different densities of singlet and triplet excitons. For example, organic electrical devices can generate excited states by injecting electrons and holes from either side of a device with random spin orientations, and if there are no other spin-dependent processes in the resulting dynamics, those electrons and holes end up as triplet excitons three times as often as they end up as singlet excitons, due to the different degeneracy of singlet and triplet spin states. This effect, and the nature of optical emission from these excited states, has a dramatic effect on the properties of organic light emitting diodes (OLEDs).

The two basic types of luminescence in organic semiconductors, fluorescence and phosphorescence, are intrinsically spin-dependent processes and thus may be modified by the effect of applied magnetic fields on the spins of nonequilibrium excitations in the materials. Fluorescence is optical emission from the $S_1$ state to the ground-state singlet ($S_0$). Fluorescence can occur without a spin flip, and thus is often quite rapid and efficient. Emission from the $T_1$ state to $S_0$ requires a spin flip, and thus occurs more slowly; it is referred to as phosphorescence. The large exchange splitting found for excitons in small molecules strongly suppresses thermally-mediated transitions from the excited triplet $T_1$ state to the excited singlet $S_1$ state. Those triplet excitons thus must recombine nonradiatively and do not contribute substantially to the electroluminescence from an OLED.\textsuperscript{15} This loss of triplet excitons has been a major motivation to explore additives called phosphors, such as heavy metals, that relax spin conservation in OLEDs. These phosphors increase the OLED emission efficiency, but at an additional expense. An alternate approach is to reduce the singlet-triplet energy splittings by using organic molecule blends, allowing triplets to convert to singlets through various mechanisms (with the help of thermal activation to overcome $\Delta_{ST}$) in an
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approach referred to as thermally-activated delayed fluorescence (TADF).

Aside from excitons, other correlated electron complexes exist and influence the optical emission from organic semiconductors. There are polaron pairs, which are electron and holes localized on distinct and separated molecules (“sites”). Their spatial separation leads to a very small wave function overlap and, therefore, a very small exchange energy relative to room temperature thermal energies. Thus the energetic obstacle to $S \leftrightarrow T$ singlet/triplet transitions is readily overcome, although the spin selection rule obstacle remains. Considerable research on magnetic field effects (primarily magneto-transport or magneto-luminescence) in organic semiconductors over the last decade focuses on ‘spin mixing’ in the polaron pair stage and how it affects exciton or bipolaron formation.\textsuperscript{16–23} The theory of these phenomena is described in detail in other chapters in this book. Here we focus on mixtures of molecules with either a low ionization potential or a high electron affinity, commonly co-evaporated together; these two types of molecules are known as donors and acceptors respectively, and the excitations of these mixtures are known as exciplexes.

1.2. \textit{Exciplex excitation and luminescence in donor-acceptor blends of organic semiconductors}

In blends of organic molecules the energetic level of the HOMO and the LUMO can be independently controlled. For donor and acceptor molecules positioned near one another, such as during co-evaporation, electron-donor-acceptor complexes form. These complexes generally have lower energy than individual excited molecules because the electron and hole can delocalize to an extent across the two molecules. When this molecule pair is excited, the complex is called an excited state complex or more succinctly an \textit{exciplex}. The delocalization (or resonance) effect reducing the excitation energy occurs even for two identical molecules, for which the excitation is known as an excimer.

For large differences in the energies of the HOMO and LUMOs between the donor and acceptor molecules, an excited complex is
likely to be characterized by charge transfer, in which the electron and the hole reside predominately on different molecules. This type of exciplex is the charge transfer (CT) excitation.\textsuperscript{24,25} For a charge-transfer excitation the spatial separation between the electron and hole can be independently determined by the donor and acceptor molecular structure, and thus the singlet-triplet exchange energy $\Delta_{ST}$ can be substantially reduced. To visualize this effect the ground state molecular orbital energies of donors ($D$) and acceptors ($A$) are shown side-by-side in Fig. 3(a).

In general the wave function of the exciplex can be written as

$$\Psi_{\text{exciplex}} = c_1 \psi(DA) + c_2 \psi(DA^*) + c_3 \psi(D^+A) + c_4 \psi(D^+A^-)$$  \(1\)

where $D^*A$ and $DA^*$ are complexes of an excited $D$ or $A$ state with a corresponding $A$ or $D$ ground state, $DA$ is the complex with both $D$ and $A$ in their respective ground states, and $D^+A^-$ is the charge transfer excitation. These four different contributions are shown in Fig. 3. The ground state is shown in Fig. 3(a) and the excited donor and acceptor states are shown in Fig. 3(bc). Figure 3(d) shows the CT orbital diagram; it is this configuration that gives rise to the magnetic field effects that are highlighted in this chapter. Although the term exciplex applies to Fig. 3(bcd) the lowest-energy exciplex (and the one with large magnetic field effects) is Fig. 3(d), and thus the term exciplex is often used synonymously with the CT complex.\textsuperscript{26} Just as with excitons, the CT excitations can be either singlet or triplet.
and an equivalent energy diagram to that of Fig. 2 can be drawn with the exception that $\Delta_{ST}$ can now be $<100$ meV for appropriately chosen $D$ and $A$ constituents. Emission from the CT state of Fig. 3 occurs when the extra electron from the $A^-$ molecules recombines with the positive hole on the $D^+$ molecule thus emitting radiation. For convenience, and to be consistent with earlier literature, from now on in this chapter we use the term exciplex and CT state interchangeably.

1.3. Spin mixing in emission from organic semiconductors

In addition to radiative transitions (such $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$), an understanding of photochemistry also requires study of radiationless (or, nonradiative) transitions. Transitions that can occur radiatively can also occur nonradiatively, and in addition there are new processes such as $S_n \rightarrow S_1$, $T_n \rightarrow T_1$, and $S_1 \leftrightarrow T_1$. It is these latter transitions that are of particular importance when spin statistics is relevant because the timescales of recombination for $S_1$ and $T_1$ are vastly different. The term “spin mixing” is generically used for these types of transitions. More specifically, $S_1 \rightarrow T_1$ is an “intersystem crossing” (ISC) and $T_1 \rightarrow S_1$ is a “reverse intersystem crossing” (RISC), although both are sometimes referred to as intersystem crossings. The fluorescence from materials that allow such spin mixing often exhibits two timescales. In “prompt” fluorescence the initially created singlets recombine radiatively, whereas spin mixing allows triplets to convert to singlets and emit via fluorescence at a later time (“delayed” fluorescence).

These intersystem crossings can occur through ordinary thermal processes, if the exchange splitting between $T_1$ and $S_1$ are comparable to or smaller than the thermal energy. The spin non-conserving process can occur via spin-orbit scattering, inhomogeneous hyperfine interactions, and other sources of different electron and hole precession frequencies. These different precession frequencies can occur in a uniform magnetic field through differences in the Landé $g$ factors, which also traces back to spin-orbit coupling, or through inhomogeneous magnetic fields (such as fringe fields from a ferromagnet with
Fig. 4. Schematic of OLED with an emissive region consisting of a $D - A$ blend. Electrons are injected from the cathode into the acceptor LUMO and holes from the anode into the donor HOMO. Electrons and holes meet in the interior as either singlet or triplet exciplexes. When the electrons and holes recombine (from singlets) light is emitted. Intersystem and reverse intersystem crossings (ISC and RISC) convert singlet and triplets into one another. Motivated by Ref. 27.

inhomogeneous magnetization, commonly coming from magnetic domains. In each of these cases the effect can be referred to as thermally-activated delayed fluorescence, and large magnetic-field effects should be expected in the fluorescence efficiency.

Figure 4 sketches an OLED that is based on emission from exciplexes. Exciplex emission is enhanced by coevaporating $D$ and $A$ molecules so that they are frequently adjacent to one another. Electrons and holes meet at $DA$ interfaces as part of either the singlet or triplet manifold. If any spin mixing occurs it does so before recombination or dissociation.

2. Thermally-Activated Delayed Fluorescence (TADF)

Investigations of the phenomenon of thermally-activated delayed fluorescence (TADF),\textsuperscript{24,28–30} which is delayed fluorescence from a thermally-activated reverse intersystem crossing, have accelerated in the past half decade after indications\textsuperscript{31,32} that the effect might
provide a practical avenue to improve OLED emission efficiency and speed without requiring heavy metal phosphors. Early phenomenological work on TADF suggested that the intersystem crossing rate \( k_{\text{ISC}} \) and reverse intersystem crossing rate \( k_{\text{RISC}} \) were proportional to their thermal equilibrium populations such that

\[
k_{\text{RISC}} = \frac{k_{\text{ISC}}}{3} e^{-\Delta \text{ST}/k_B T}.
\]

An effective second rate of (delayed) fluorescence, \( k_{\text{TADF}} \), caused by triplet states converting to singlet and then recombining is limited by \( k_{\text{RISC}} \):

\[
k_{\text{TADF}} = \frac{k_S}{3} e^{-\Delta \text{ST}/k_B T},
\]

where \( k_S \) is the rate of fluorescence. \(^{33}\) The processes leading to \( k_{\text{RISC}} \) and \( k_{\text{ISC}} \) must depend on spin if the spin multiplicity is to be changed; the natural mechanism for the conversion process is the spin-orbit interaction, although hyperfine interactions can also mediate the transitions. ISC \( (S_1 \rightarrow T_1) \) typically occurs by spin-orbit coupling to a vibronic \( T_1 \) level or some other excited \( T_n \) level which then may decay down to \( T_1 \). \(^{24}\)

\section*{2.1. Orbital states and TADF}

Careful consideration of the nature of the orbital states involved in the intersystem crossings relevant to TADF is required. For electron-hole separations that are large enough that the exchange energy is very small compared with the intramolecular excitation energies [corresponding to the right-hand side of Fig. 2(a)], then the electron and hole wave functions that enter into the triplet and singlet exciplex wave functions are nearly identical. The El-Sayed rules\(^ {34}\) dictate that spin-orbit matrix elements do not yield large transition rates between such singlet and triplet exciplexes. As the electron and hole move together, towards the left-hand side of Fig. 2(a), then the exciplex energies for singlet and triplet can differ substantially and as a result the electron and hole wave functions are also modified. Thus the spin-orbit-induced coupling between the singlet
and triplet exciplexes will increase, producing more rapid intersystem crossings.

However, as indicated in Fig. 2, there are a range of possible excitation characteristics for the electron and hole, as well as for the vibrational excitations of the two molecules. These often mix into vibronic states in which the reduced wave function overlap of singlets and triplets with differing vibrational character is compensated by the increased overlap of the orbitals (due to a relative displacement of electron and hole wave functions for triplet and singlet excitations that breaks the assumptions of the El-Sayed rules). Such considerations also motivate the suggestion in some models for TADF that the intersystem crossings occur through an intermediary local triplet excitation (which could be on either a donor or acceptor)\textsuperscript{35} which is vibronically coupled to the triplet exciplex.\textsuperscript{33} As a much larger spin-orbit coupling exists between a local excitation and the intermolecular excited states,\textsuperscript{36} this provides motivation for large TADF rates.

In our analysis it is not essential that the relevant triplet state that spin mixes with the singlet excited state is the $T_1$ state, or even that the relevant states are exciplex states; the key feature which justifies our analysis is that the relevant energy scale for the intersystem crossing is much smaller than for excitons (and comparable to the thermal energy), and that TADF is demonstrated in the experimental system explored. TADF itself is only possible if the El Sayed rules do not apply to the relevant singlet and triplet excitations which enter into the intersystem crossings. We note that the El Sayed rules do not apply to some other mechanisms of converting between singlet and triplet excitations, such as hyperfine interactions or differences in the Landé $g$ factor, and thus magnetic-field effects on TADF may use different singlet-triplet conversion channels than zero-magnetic-field TADF.

\textbf{2.2. A simple model of TADF}

We now present a simple model of TADF which will illustrate the main features and identify some subtleties, but without the multitude of additional states that can be required to describe
some experimental situations quantitatively. This analysis also foreshadows the formalism to be used in later sections. We consider populations of singlet and triplet charge transfer states or exciplexes which are represented by a spin density matrix $\rho$ described by the following equation

$$\frac{\partial \rho}{\partial t} = -\frac{1}{2} (k_S P_S + k_T P_T, \rho) + L_{ISC}\rho L_{ISC}^\dagger - \frac{1}{2} \{L_{ISC}^\dagger L_{ISC}, \rho\}$$

$$+ L_{RISC}\rho L_{RISC}^\dagger - \frac{1}{2} \{L_{RISC}^\dagger L_{RISC}, \rho\},$$

(4)

where $L_{ISC} = L_{S\to T} = \sqrt{k_{ISC}} \langle T|S\rangle$ and $L_{RISC} = L_{T\to S} = \sqrt{k_{RISC}} \langle S|T\rangle$ are Lindblad operators that describe the (reverse) intersystem crossings between singlets and triplets. The curly brackets denote anticommutation. The average population of singlets (triplets) are then determined by

$$n_S = \text{Tr} P_S \rho \quad (n_T = \text{Tr} P_T \rho)$$

where $P_S$ and $P_T$ are singlet and triplet projection operators, respectively. Using these relations the temporal dynamics appears in a more familiar rate equation form:

$$\frac{d}{dt} \begin{pmatrix} n_S \\ n_T \end{pmatrix} = \begin{pmatrix} -(k_S + k_{ISC}) n_S + k_{RISC} n_T \\ -(k_T + k_{RISC}) n_T + k_{ISC} n_S \end{pmatrix}.$$  

(5)

Studies of TADF frequently use time-dependent measurements of photoluminescence; the initial condition for optical excitation is

$$\rho(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix},$$ 

(6)

(i.e. all initial states are spin singlet). Although the differential equations above can be solved analytically, the full expressions are not very transparent and in any case desirable TADF properties require the parameters to reside in the regime $k_S \gg k_{ISC}, k_{RISC}, k_T$, which reduces the complexity of the solutions. The solutions for the two populations are then

$$n_S(t) = n_S(0)e^{-(k_S+k_{ISC})t} + \frac{k_{RISC} n_T^*}{k_S} e^{-(k_T+k_{RISC})t},$$

(7)

$$n_T(t) = n_T^* e^{-(k_T+k_{RISC})t} - n_T e^{-(k_S+k_{ISC})t},$$

(8)
where \( n_T^* = k_{ISC} n_S(0) / k_S \) is the population of triplets after the prompt fluorescence has finished. At sufficiently long times

\[
\begin{align*}
n_S(t > 1/k_S) &= \frac{k_{RISC} n_T^*}{k_S} e^{-(k_T + k_{RISC})t}, \\
n_T(t > 1/k_S) &= n_T^* e^{-(k_T + k_{RISC})t},
\end{align*}
\]

(9)

which is the regime of delayed fluorescence. Figure 5 shows the distinct time dependence for the prompt and delayed fluorescent components for excitation at \( t = 0 \).

The fluorescence in the steady state is found by solving

\[
\begin{align*}
\frac{\partial \rho}{\partial t} &= 0 = -\frac{1}{2} \{ k_S P_S + k_T P_T, \rho \} + L_{ISC} \rho L_{ISC}^\dagger - \frac{1}{2} \{ L_{ISC} L_{ISC}^\dagger, \rho \} \\
&\quad + L_{RISC} \rho L_{RISC}^\dagger - \frac{1}{2} \{ L_{RISC} L_{RISC}^\dagger, \rho \} + G
\end{align*}
\]

(10)

where \( G \) is a generation term which, for photoluminescence, applies only to the singlet population. For continuous-wave (cw) excitation,

\[
G = \begin{pmatrix} G_S & 0 \\ 0 & 0 \end{pmatrix}.
\]

(11)

Fig. 5. Fluorescence decay in time showing the prompt decay and the delayed decay using \( k_{ISC} = 0.01 \mu s^{-1}, k_{RISC} = k_{ISC}/10, k_S = 0.32 \mu s^{-1}, \) and \( k_T = 0.027 \mu s^{-1} \). The sharper decay after the delay is due to nonradiative transitions via \( k_T \). Phosphorescence is not included in the model for emission (only emission from singlets is shown here). The black curve is the exact analytic calculation and the orange dashed curve is an approximate calculation of Eq. (7).
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For general rates

\[ n_S(t \to \infty) = G_S \frac{k_{RISC} + k_T}{k_S(k_{RISC} + k_T) + k_T k_{ISC}}, \]  
(12)

\[ n_T(t \to \infty) = G_S \frac{k_{ISC}}{k_S(k_{RISC} + k_T) + k_T k_{ISC}}. \]  
(13)

If \( k_{RISC} \) is the smallest rate \( (k_{RISC} \ll k_T) \), which is the low temperature regime [Eq. (2)], then

\[ n_S(t \to \infty) = \frac{G_S}{k_S + k_{ISC}}. \]  
(14)

We are chiefly concerned with the singlet population, because the intensity of light emission depends centrally on it. At high enough temperatures \( (k_{RISC} \gg k_T) \) the singlet population becomes independent of temperature \( (n_S \sim G_S/k_S) \).

The density matrix formalism provides a convenient way to focus on transitions between different spin states in an environment within which transitions between different orbital and vibrational states are very rapid compared to spin mixing. The reduction of the density matrix of the entire system to a two-spin-channel model is justified when the transitions between the spin channels are much slower than any transitions within the channels. Thus the triplet channel should not be considered to be one specific triplet eigenstate, and the singlet channel should not be considered to be one specific singlet eigenstate. Various scattering events will efficiently and rapidly mix individual singlet eigenstates with other singlet eigenstates, but this does not necessarily need to be tracked within this density matrix formalism. Thus it is also not necessary to specifically identify which triplet states are converted into singlet states via the Lindblad operator; it is sufficient to know that there is some coupling, and that this coupling is weak compared with the scattering rates within the singlet channel and within the triplet channel, in order to formulate the density matrix expression in this fashion.

For example, recent in-depth experiments\(^{35,38}\) have led to new understandings of the processes and specific states that lead to TADF at zero magnetic field. The pivotal conclusion is that singlet-triplet
spin mixing of charge transfer or exciplex states occurs not directly between those singlet and triplet levels but instead via intermediate local excited states (e.g. either $3LE_D$ or $3LE_A$) which are vibronically coupled to the CT/exciplex states. Although these most recent advancements in understanding zero-field TADF have yet to be incorporated into existing models of the magnetic-field effects on TADF, they do not invalidate the general density matrix approach as the nature of the states involved are still specifically triplet or singlet, and the processes involved still involve intersystem and reverse intersystem crossings.

2.3. Comparison with electron spin relaxation rates

A similar two-component density matrix treatment is frequently done for electron spin decoherence in conduction states in III-V semiconductors and quantum wells, through an analysis known as D’yakonov-Perel’ spin relaxation.\textsuperscript{4,39–41} Here the density matrix is written for the conduction electron spin-up and conduction electron spin-down channels, which are coherently mixed by spin-orbit interaction rates that are very much smaller than the orbital scattering rates or the range of thermally-occupied energies the conduction electrons explore. One difference between the singlet-triplet dynamics and the spin-relaxation dynamics in III-V semiconductors is the role of the singlet-triplet energy splitting, which quenches any transitions for triplets to singlets for energies below the singlet energy. A similar role would be played by a Zeeman energy splitting in spin relaxation, but the consequences of such an effect are usually dominated by orbital magnetic field effects.\textsuperscript{40,41} For the zero-field case considered above the effect of this splitting is simply to reduce the effective RISC rate by the thermal occupation factor, as only those states above the singlet energy threshold can produce RISC. The effect on magnetic-field-induced dynamics will be examined later.

3. Theory of Organic Magneto-Electroluminescence

The emission from either excitonic or charge transfer states is determined by solving for the spin density matrix $\rho$ which evolves
according to the stochastic Liouville equation (SLE):\textsuperscript{42–47}

\[
\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}, \rho] - \frac{1}{2} \{k_S P_S + k_T P_T, \rho\} - k_D \rho + \hat{G} \quad (15)
\]

where \( P_S \) and \( P_T \) are

\[
P_S = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad P_T = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.
\]

\( k_D \) is a spin-independent dissociation rate and \( \hat{G} \) is the pair-generation matrix. The density matrix is 4x4 with basis states of singlet and triplet polaron pairs for excitonic emission and of singlet and triplet exciplexes for exciplex emission.

For the exciton model, the spin mixing is occurring between polaron pairs, and thus it is assumed that the generation matrix is diagonal with elements \( G_S = G_T \), as there is no singlet-triplet gap for polaron pairs. For exciplexes the generation matrix is:

\[
\hat{G} = \begin{pmatrix} G_S & 0 & 0 & 0 \\ 0 & G_{T^*} & 0 & 0 \\ 0 & 0 & G_{T^*} & 0 \\ 0 & 0 & 0 & G_{T^*} \end{pmatrix},
\]

where \( G_{T^*} \) is the number of triplet exciplexes generated in the triplet channel at energies that exceed \( \Delta_{ST} \). Exciplexes are generated in the entire triplet channel as well, with a rate \( G_T \), but only those whose energies exceed \( \Delta_{ST} \) participate in the spin mixing. Thus a temperature dependence characteristic of TADF enters through \( G_{T^*} = G_T e^{-\Delta_{ST}/k_B T} \). If the exciplexes are formed from polaron pairs then \( G_T \) and \( G_S \) from electrical injection should be comparable. All rates introduced are identified on Fig. 6, which shows a Jablonski energy diagram for exciplexes.
Fig. 6. Exciplex Jablonski diagram. The Jablonski diagram for excitons looks identical except $\Delta_{ST}$ is much larger for exciplexes, which precludes any thermally-occupied $T^*$ states at typical temperatures.
The Hamiltonian of the polaron pair or exciplex is $\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{HF} + \mathcal{H}_{FF} + \mathcal{H}_{HF,\delta g} + \mathcal{H}_{FF,\delta g}$ where

$$
\mathcal{H}_Z = \frac{g_1 + g_2}{2} \mu_B B_0 \cdot (S_1 + S_2)
+ \frac{g_1 - g_2}{2} \mu_B B_0 \cdot (S_1 - S_2),
$$
(16)

$$
\mathcal{H}_{HF} = \frac{g_1 + g_2}{2} \mu_B \left( B_{HF}(r_1) \cdot S_1 + B_{HF}(r_2) \cdot S_2 \right),
$$
(17)

$$
\mathcal{H}_{FF} = \frac{g_1 + g_2}{2} \mu_B \frac{B_{FF}(r_1) + B_{FF}(r_2)}{2} \cdot (S_1 + S_2)
+ \frac{g_1 - g_2}{2} \mu_B \frac{B_{FF}(r_1) - B_{FF}(r_2)}{2} \cdot (S_1 - S_2),
$$
(18)

$$
\mathcal{H}_{HF,\delta g} = \frac{\delta g}{2} \mu_B \left( B_{HF}(r_1) \cdot S_1 - B_{HF}(r_2) \cdot S_2 \right),
$$
(19)

$$
\mathcal{H}_{FF,\delta g} = \frac{\delta g}{2} \mu_B \frac{B_{FF}(r_1) + B_{FF}(r_2)}{2} \cdot (S_1 - S_2)
+ \frac{\delta g}{2} \mu_B \frac{B_{FF}(r_1) - B_{FF}(r_2)}{2} \cdot (S_1 + S_2);
$$
(20)

where $B_{HF}$ is the hyperfine field, $r_{1,2} (S_{1,2})$ are the positions (spins) of the two constituents, and $\delta g = g_1 - g_2$. The fringe field Hamiltonian ($\mathcal{H}_{FF}$) and its associated $\delta g$ factor counterpart ($\mathcal{H}_{FF,\delta g}$) are only relevant when inhomogeneously magnetized magnets are in proximity to the active area. We neglect $\mathcal{H}_{HF,\delta g}$ and $\mathcal{H}_{FF,\delta g}$ as of higher order compared to $\mathcal{H}_Z$, $\mathcal{H}_{HF}$, or when appropriate, $\mathcal{H}_{FF}$. Figure 7(a) shows a physical representation of an exciplex on adjacent donor and acceptor molecules. Figures 7(b), (c) are schematics of the $\delta g$ and hyperfine interactions. Further description of the $\delta g$ mechanism provided in the next section while other Chapters cover the hyperfine interaction in detail. We now describe the solutions to these equations for various models appropriate to different material regimes.

3.1. The $\delta g$ mechanism

The formalism thus presented can be overwhelming given the number of terms in the SLE, and the number of possible spin interaction Hamiltonians. In general numerical solutions to the SLE are
necessary. However if all interactions except for $\mathcal{H}_Z$ are ignored, analytic solutions are possible. Aside from being merely tractable, such a situation appears to arise in certain donor-acceptor blends.\textsuperscript{47,51,52}

A very simple analysis will first be presented, followed by the applications to specific cases with some additional rates included.

The central physics can be understood by focusing on two states, the $S$ and $T_0$ states, which are coupled through the different Landé $g$ factors of the electron and hole that comprise them:

$$\mathcal{H}_{\delta g} = \frac{\delta g}{2} \mu_B \mathbf{B} \hat{z} \cdot (\mathbf{S}_e - \mathbf{S}_h).$$

When this term is commuted with the two-channel density matrix,

$$\rho = \begin{pmatrix} \rho_{SS} & \rho_{ST_0} \\ \rho_{T_0S} & \rho_{T_0T_0} \end{pmatrix}$$

\textbf{Fig. 7.} (a) Schematic of an exciplex. (b) Spin mixing due to variations in the Landé $g$-factor. (c) Spin mixing due to the hyperfine interaction. Taken from Ref. 47.
to determine an equation of motion, we obtain

\[
\frac{\hbar}{i} \frac{\partial}{\partial t} \begin{pmatrix}
\rho_{SS} & \rho_{ST_0} \\
\rho_{T_0S} & \rho_{T_0T_0}
\end{pmatrix}
= iB \delta g \mu_B \begin{pmatrix}
(\rho_{ST_0} - \rho_{T_0S}) & (\rho_{SS} - \rho_{T_0T_0}) \\
-(\rho_{SS} - \rho_{T_0T_0}) & -(\rho_{ST_0} - \rho_{T_0S})
\end{pmatrix}
\]

(23)

The dynamics expressed by this equation can be succinctly summarized by noting that the rate of change of the off-diagonal terms (e.g. \(\rho_{ST_0}\)) is related to the difference of the diagonal terms (which are the populations of singlets and triplets), and the rate of change of the diagonal terms (e.g. \(\rho_{SS}\)) is related to the difference of the off-diagonal terms. Thus the enhancement with magnetic field of the luminescence from the singlet population, \(k_S \rho_{SS}\), will be proportional to the magnetic field squared. If the initial condition corresponded to a generated population on the diagonal of the density matrix at a specific time \((t = 0)\) then for subsequent times the off-diagonal term grows linearly in time and magnetic field. Similarly one then expects magnetic-field-dependent changes in the diagonal terms that are linear in the time and magnetic field, multiplying the off-diagonal terms; this yields a magnetic field effect on the diagonal that is the square of the magnetic field and the square of the time. Physically this can be viewed as the consequence of two initially parallel spins (thus in a triplet configuration) which precess at a different rate and thus end up in a linear superposition of parallel and antiparallel configurations as shown in Fig. 7(b). The steady-state solution for low-field MEL, when generation and other rates are included, is reported in the sections below. It can be useful to consider the physical nature of this two-spin precession. The eigenstates of the \(\delta g\) Hamiltonian are \(|\uparrow\downarrow\rangle\) and \(|\downarrow\uparrow\rangle\), and the time evolution of a \(T_0\) state in the presence of that Hamiltonian is

\[
|\Psi\rangle = e^{i\delta g \mu_B Bt/2} |\uparrow\downarrow\rangle \sqrt{2} + e^{-i\delta g \mu_B Bt/2} |\downarrow\uparrow\rangle \sqrt{2}
\]

(24)

\[
= e^{i\delta g \mu_B Bt/2} (|T_0 \rangle + |S \rangle)/2 + e^{-i\delta g \mu_B Bt/2} (|T_0 \rangle - |S \rangle)/2
\]

(25)
We now return to our consideration of the effect of the singlet-triplet splitting, $\Delta_{ST}$ on the MEL. Two scenarios are consistent with survival of the MEL in the presence of a substantial singlet-triplet splitting. In the first, the timescale for energy changes in the triplet state is long compared with the precession time between singlet and triplet. As the precession times are of order microseconds, and the vibrational scattering times are likely much shorter than picoseconds, this regime appears implausible. An alternate version in which the MEL occurs while the triplet state is in a stable excited configuration, such as a local triplet exciton, might be possible. More likely, however, is that the triplet/singlet coherent state is largely unaffected by the temporary difference in energy between triplet and singlet, as the two precess. Relative excursions in the singlet and triplet energies may produce dynamical phase differences between triplet and singlet in Eq. (25), which appear as an additional time-dependent phase

$$\Psi = e^{i\delta g \mu_B B t/2} (|T_0 > + e^{i\theta(t)} |S >) / 2 + e^{-i\delta g \mu_B B t/2} (|T_0 > - e^{i\theta(t)} |S >) / 2. \quad (26)$$

If the $T_0$ and $S$ manifolds that are tracked in the density matrix treatment (i.e. those states within the manifolds that can be mixed by the spin-orbit interaction) are selected so that they have the same average energy (discarding the low-energy triplet states that cannot be mixed with the singlet states), then $\theta(t)$ will average to zero, and the magnetic field effects on the relative populations of $T_0$ and $S$ will be unaffected. This phenomenon is very different from the role of scattering in, for example, spin relaxation in conduction electrons in III-V semiconductors. There the dephasing of different spins relative to the overall population, followed by scattering that scrambles the orbital information, is central to the motional narrowing regime for electron spin relaxation.

3.1.1. The exciton picture

We first examine situations where the eventual emissive recombination stems from excitons (intramolecular pairs) instead of exciplexes
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(intermolecular pairs). The difference between the two is that the S-T splitting, \( \Delta_{ST} \), is much larger for excitons (\( \sim 1 \text{ eV} \gg \sim 50 \text{ meV} \)). Such a large splitting precludes any spin mixing with the exciton spin states (so for all intents and purposes \( \delta g = 0 \)). Moreover the negative and positive polarons are tightly bound (binding energy \( E_B \gg k_B T \)) which suppresses any exciton dissociation into polaron pairs (\( k_D = 0 \)).

The SLE of Eq. (15) is then solved in the steady state. By considering only fluorescence (emission from singlets excitons), the quantity of interest is \( \text{Tr} \rho_P S \)

\[
MEL = \frac{\text{Tr} \rho_P S(B_0) - \text{Tr} \rho_P S(B_0 \rightarrow 0)}{\text{Tr} \rho_P S(B_0 \rightarrow 0)}
\]

which for this case yields

\[
MELo = \left[ \frac{k_S - k_T}{2k_D + k_S + k_T} \right] \frac{(\delta g \mu_B B/h)^2}{(k_D + k_T)(k_D + k_S) + (\delta g \mu_B B/h)^2}.
\]

Note that the width of the Lorentzian function scales as \( \sqrt{(k_D + k_S)(k_D + k_T)/\delta g} \approx \sqrt{k_S k_T/\delta g} \). The bracketed expression gives the high-field MEL.

3.1.2. The exciplex picture

If the emissive precursors are exciplexes instead of excitons, the much smaller exchange energy (\( \Delta_{ST} \sim k_B T \)) allows spin mixing within the exciplex manifold. A consideration of that spin mixing provides

\[
MEL = \left[ G_{T^*}(k_S + k_D) - G_S(k_T + k_D) \right] \frac{(\delta g \mu_B B/h)^2}{G_S(2k_D + k_S + k_T)}
\]

which has the same form as the excitonic MEL in Sec. 3.1.1 if \( G_{T^*} = G_S \). An activated (Arrhenius) temperature dependence for the MEL follows from Eq. (29) for \( G_{T^*} = G_T e^{-\Delta_{ST}/k_B T} \) and \( G_T = G_S \), so long as \( (k_S + k_D)e^{-\Delta_{ST}/k_B T} > k_T + k_D \). Thus mathematically there is no difference between the exciton and exciplex results, however the rates
Fig. 8. Percent MEL versus applied magnetic field for exciplexes (black, blue, red), using Eq. (29), and excitons (dashed green), using Eq. (28). The exciplex curves are labeled by their ratio of exchange splitting to temperature. The following values were used; exciplex: $k_S = 1 \times 10^{-4}$ ns$^{-1}$, $k_T = 1 \times 10^{-5}$ ns$^{-1}$, $k_D = 1 \times 10^{-6}$ ns$^{-1}$, $\delta g = 1 \times 10^{-4}$; exciton: $k_S = 1 \times 10^{-1}$ ns$^{-1}$, $k_T = 2 \times 10^{-1}$ ns$^{-1}$, $k_D = 0$, $\delta g = 1 \times 10^{-4}$.

$k_i$ differ in value and in physical process described, as summarized in Table I.

Figure 8 displays the MEL (in %) as a function of applied magnetic field. For excitons (green dashed curve), $k_S \approx k_T$ and these rates are much larger than what is found for exciplexes. No temperature dependence is visible as excitons are formed after spin mixing occurs between polaron pairs, and there is negligible spin splitting between singlet and triplet polaron pairs. The size of $k_S$ and $k_T$ lead to much larger widths in the magnetic-field dependence of the MEL than what is found for the exciplexes (black, blue, and red curves). Exciplex line shapes are shown for different ratios of spin splitting to temperature; the large temperature dependence of the MEL is clearly present.

3.2. Magnetoelectroluminescence from $\delta g$ and hyperfine interactions

When analyzing MEL curves in realistic materials the influence of both the $\delta g$ mechanism and the hyperfine mechanism should be considered. Figure 9 shows the high-field MEL percentage of the $\delta g$ mechanism (a) and the hyperfine mechanism (b). The hyperfine
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Fig. 9. (a) Theoretical calculations for the MEL at large field with the $\delta g$ mechanism ($B_{0hf} = 0$). (b) Theoretical calculations for the MEL from hyperfine spin mixing at large field ($\delta g = 0$). Increasing either $G_T/G_S$ or $B_{0hf}$ causes the MEL to be more negative. Orange lines are $G_T = G_S = 0.25$ and black lines are $G_T = G_S = 1$. From Ref. 47.

curves are calculated assuming that semiclassical hyperfine fields are Gaussian distributed with width $B_{0hf}$. These two plots apply equally to excitons and exciplexes. For excitons the regime of validity is near $k_T/k_S \approx 1$ where the MEL is small and the MEL sign hinges on the relative size of the two formation rates. For exciplexes the regime of validity is near $k_T/k_S \ll 1$ where the MEL is large in either case ($\delta g$ or hyperfine) but the sign is dependent on the dominant mechanism, which greatly assists assigning the correct mechanism to the MEL of exciplex recombination.

3.3. Magneto-photoluminescence

Magneto-photoluminescence (MPL) can be covered within this theory as well, by taking $G_T = 0$ and $G_S$ finite due to optical excitations. It is evident from Eq. (29) that MPL $< 0$; at least one experiment has viewed negative MPL but others have observed MPL $> 0$. m-MTDATA/3TPYMB (1:1) has shown both signs. The model of Eq. (29) assumes that the $\delta g$ mechanism is solely responsible for spin mixing. This cannot be the complete picture, for TADF is observed in the absence of an applied magnetic field and the $\delta g$ mechanism is ineffective without an applied magnetic field. The theory is readily generalizable to include field-independent spin mixing rates ($k_{ISC}$ and $k_{RISC}$) between $S_1$ and $T_1$ which are due to the spin-orbit interaction. The SLE then
becomes

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}, \rho] - \frac{1}{2}\{k_S P_S + k_T P_T, \rho\} - k_D \rho + \hat{G}
+ \sum_{i=1}^{6} \left( L_i \rho L_i^T + L_i \rho L_i^T - \frac{1}{2} \{L_i^T L_i + L_i^T L_i, \rho\} \right)$$

where \( L_i \) is the Lindblad operator that sends state \( i \) to another state \( j \neq i \). For instance \( L_1 = L_{S \rightarrow T^*_0} = \sqrt{k_{ISC}} |T^*_0\rangle \langle S| \). The solution for the MPL is long but it can be shown that MPL > 0 if \( k_{ISC} > k_D + k_T + k_{RISC} \). ISC and RISC also have effects on MEL, and the MEL can surpass 100% if \( k_{ISC} \) becomes comparable to and then larger than \( k_S \). The reason for this enhancement is that the fluorescence from initial singlets is reduced and only regained through \( \delta g \) spin mixing (assuming that \( k_{RISC} \) is very small compared to \( k_{ISC} \)).

Approximate values of \( k_{ISC} \) are \( 1 - 10 \times 10^{-4} \) ns\(^{-1}\). The analysis of Hontz et al. for a 1:1 blend of m-MTDATA:3TPYMB indicates \( k_{ISC} = 140 \times 10^{-6} \) ns\(^{-1}\), which in our model yields an MEL \( \approx 3.5\% \). An intersystem crossing rate one-tenth that yields an MEL \( \approx 26\% \).

3.4. **Exciplex dynamics with separate \( T \) and \( T^* \) levels**

A more sophisticated model is produced when excitation and de-excitation between the \( T \) and \( T^* \) levels is included explicitly. Some immediate consequences of this theory will be described here, as an example of the behavior of this system in the presence of additional related states. The Lindblad operators describing transitions between these states appear in the stochastic Liouville equation in the following way:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}, \rho] - \frac{1}{2}\{k_S P_S + k_T P_T, \rho\} - k_D \rho + \hat{G}
+ \sum_{i=T_0,T_+,T_-} \left( L_i(u) \rho L_i(u)^T + L_i(d) \rho L_i(d)^T
- \frac{1}{2} \{L_i(u)^T L_i(u) + L_i(d)^T L_i(d), \rho\} \right)$$
where $L_i(u)$ is the Lindblad operator that sends an electron up in energy from $T_i$ to a vibrational state $T_i^*$ and $L_i(d)$ sends an electron down in energy from the vibronic level $T_i^*$ to $T_i$. The Lindblad operators, $L_i$, describe different rates of population shuffling within the system. For instance $L_{T_0}(u) = L_{T_0 \rightarrow T_0^*} = \sqrt{k_{up}} |T_0^* \rangle \langle T_0|$, $L_{T_+}(d) = L_{T_+ \rightarrow T_+^*} = \sqrt{k_{down}} |T_+^* \rangle \langle T_+|$. There are six possible incoherent transitions encompassed in the Lindblad terms. These rates, $k_{up}$ and $k_{down}$ are assumed to be spin independent and related by a Boltzmann factor such that $k_{up} = k_{down} e^{-\Delta/k_B T}$, where $\Delta$ is the energy separation between $T_1$ and a specific vibronic level. Our chief consideration is that the vibronic triplet levels $T^*$ that are resonant with $S$ are added to the model, so $\Delta = \Delta_{ST}$. The generation matrix, basis vector, and projection operators are now

$$\hat{G} = \begin{pmatrix}
G_S & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & G_T & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & G_T & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & G_T
\end{pmatrix}, \quad \begin{pmatrix}
|S\rangle \\
|T_0^*\rangle \\
|T_0\rangle \\
|T_+\rangle \\
|T_+^*\rangle \\
|T_-\rangle
\end{pmatrix},$$

$$P_S = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}, \quad P_T = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}.$$

A physical picture is shown in Figure 10. Triplets are generated at the rate $G_T$ in $T_1$ and then fluctuate between $T_1$ and the vibronic
Fig. 10. An exciplex model that explicitly includes $T \leftrightarrow T^*$ transitions.

levels of $T^*$ (with energy $E_{T^*} = E_S$) with the rates $k_{up}$ and $k_{down}$. When $T^*$ is occupied, coherent spin evolution into the $S$ state is possible. Singlets are electrically generated as well, with a rate $G_S = G_T$. $S$ states may spin mix to unoccupied $T^*$ state in which case they can fall down to $T$ states at the rate $k_{down}$. There will be vibronic singlet levels as well, though for simplicity only $S_1$ is included in the model.

The MEL can be calculated analytically though the expression is complex. In the limit of dissociation $k_D$ smaller than all other rates the maximum MEL is

$$MEL_{\text{max}} = \frac{k_S k_{up} - k_T k_{down}}{k_T k_{down} + k_S (k_T + k_{up})},$$

where it is evident that the $T^*$ states play an important role; either $k_{up}$ and $k_{down}$ must be finite if any MEL is to appear. For orbital and vibrational scattering rates that are very large compared to the other rates of the problem ($k_{up}$ and $k_{down}$ much larger than all other rates) and $k_T \ll k_S$, the thermal equilibrium within the excited triplet manifold will require $k_{up}/k_{down} \sim e^{-\Delta_{ST}/k_B T}$, and the limit of Eq. (30) is $MEL_{\text{max}} = 1$. Noteworthy is that the maximum MEL is 100%, which indicates that even though most triplets cannot spin mix
Fig. 11. (a) MEL calculated from the more sophisticated model with $k_{\text{down}} = 10^{-3} \text{ ns}^{-1}$ and $k_{\text{up}} = k_{\text{down}} \exp(-\Delta ST/k_BT)$ for three different temperatures. (b) MEL at high magnetic field calculated as a function of $\Delta ST/k_BT$ for three different $k_{\text{down}}$ and $k_{\text{up}} = k_{\text{down}} \exp(-\Delta ST/k_BT)$. Other values used are $k_S = 1 \times 10^{-4} \text{ ns}^{-1}$, $k_T = 1 \times 10^{-5} \text{ ns}^{-1}$, $k_D = 0$, $\delta g = 1 \times 10^{-4}$. No hyperfine interaction was used in these calculations.

at any given time, they will effectively be spin mixed into the singlet channel over time, so that all the $T_0$ states produce luminescence through TADF.

Theoretical results from this model are shown in Fig. 11; Figure 11(a) is the MEL for three different ratios of $\Delta ST/k_BT$. As the ratio decreases (e.g. temperature increases), the MEL increases in agreement with the several experiments with TADF materials.$^{27,47,51,52}$ Figure 11(b) shows that for low enough temperature, the model predicts the MEL to change sign since the excitation of triplets $T \rightarrow T^*$ is too weak to compete with the spin mixing of $S \rightarrow T^*$. A result $S$ becomes less populated as the applied field increases and the MEL turns negative.

4. Spin Decoherence

Transitions included to this point include those between states like $S_1$ and $S_0$, with rate $k_S$, or between $S_1$ and $T_1$, with rates of $k_{\text{ISC}}$ or $k_{\text{RISC}}$; the coherent evolution of spin from the Zeeman interaction and hyperfine interactions also appears. So far neither spin relaxation nor spin decoherence of the individual spins that make up either a polaron pair or an exciplex have been included.
Although spin relaxation (with rate $1/T_1$) is typically very weak in organic semiconductors, the spin decoherence rates ($1/T_2$) are on the order of microseconds and may contribute to the physics of these systems. Although these spin decoherence times are much slower than the dominant transition times in the excitonic model, the spin decoherence times are comparable to $1/k_S$ in the exciplex model. The previous model can be generalized to account for a finite $T_2$ for the two spins forming either a polaron pair or exciplex.

We define decoherence Lindblad operators in the Zeeman basis for each of the two spins, $L_3(1)$ and $L_3(2)$:

$$L_3(1) = \mathbf{1} \otimes L_3, \quad L_3(2) = L_3 \otimes \mathbf{1}$$

(31)

where

$$\hat{L}_3 = \sqrt{\frac{1}{2T_2}} \sigma_z.$$

Additional operators $L_1$ and $L_2$ could be included if spin relaxation were strong. To express these operators in the $S-T$ basis, the following transformation matrix is applied:

$$\hat{T} = \begin{pmatrix}
0 & 0 & 1 & 0 \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}$$

(32)

which gives new operators in the preferred basis as $\hat{T}^T L_3(j) \hat{T}$. The Lindblad operators enter the stochastic Liouvile equation as

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\{\mathcal{H}, \rho\} - \frac{1}{2}\{k_S P_S + k_T P_T, \rho\} - k_D \rho + \frac{1}{4} \hat{G} + \frac{1}{2} \{L_3(1)^T L_3(1), \rho\} + \frac{1}{2} \{L_3(2)^T L_3(2), \rho\}.$$  

(33)
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The effect of decoherence on the simple exciplex model of the MEL from the $\delta g$ mechanism explored here increases the MEL width according to

$$\Delta B = \frac{\sqrt{(2k_D + k_S + 4/T_2)(k_D k_S + (2k_D + k_S)/T_2)}}{\delta g \sqrt{2k_D + k_S}}$$  \hspace{1cm} (34)$$

with $k_D \ll k_S \sim 1/T_2$ and $G_S = G_T = G$. $k_T = 0$ here but the result can be modified slightly to account for finite $k_T$. The MEL at large field, (the saturated MEL), is now

$$\text{MEL}_{\text{sat.}} = \frac{(k_S - k_T)(k_D + k_T)}{(2k_D + k_S + k_T)(k_D + k_T + 2/T_2)}$$  \hspace{1cm} (35)$$

or

$$\text{MEL}_{\text{sat.}} = \frac{k_D + k_T}{2/T_2}$$  \hspace{1cm} (36)$$

when $k_D, k_T \ll k_S, 1/T_2$. In either case the spin decoherence reduces the overall MEL.

5. Experimental Measurements of MEL in Exciplex Materials

Early work on exciplex materials\textsuperscript{54–56} proposed hyperfine interactions to explain the MEL, and the values of MEL were not large and had various signs. For example, in a study of magnetic field effects in exciplexes using $m$-MTDATA/Bphen,\textsuperscript{56} the EL spectra confirmed exciplex emission at the donor-acceptor interface, although the donor and acceptor molecules were not coevaporated to maximize exciplex efficiency. In Ref. 56, the maximum measured MEL averaged over the emission spectrum was near 6% and was attributed to hyperfine interactions between polaron pairs; spin mixing between exciplex constituents was assumed to be energetically suppressed. The hyperfine picture is bolstered by spectrally resolved MEL measurements which showed that low energy, “cold” polarons tend to have wider MEL widths. This observation is consistent with larger hyperfine fields as $B_{hf} \propto 1/\sqrt{\text{volume}}$. The widths measured extended
from 10 mT for higher energy polaron pairs/exciplexes to 25 mT for lower energy polaron pairs/exciplexes. These widths, however, appear also to be consistent with later measurements that do not attribute the MEL to nuclear moments.

δ

spin mixing among exciplexes and hyperfine spin mixing of polaron pairs was proposed as the mechanism for subsequent work on magneto-photoluminescence and MEL in exciplex materials.\(^{51}\) The role of hyperfine spin mixing in contributing to the observed signals was not detailed. A strong temperature dependence in both the MPL and MEL was identified, and the MEL width appeared too large to support a hyperfine mechanism alone. At 300 K, the MEL surpassed 30% (38% at 317 K), making the effect one of the largest observed at the time although the values were not qualitatively larger than the largest MEL’s seen in exciton-emissive materials. The first MFEs exceeding 100% at room temperature appeared shortly thereafter.\(^{27}\) A key finding was that the blend ratio was an indicator of the size of the MFE. In this case\(^{27}\) using 75% 3TPYMB to 25% m-MTDATA was found to yield the largest responses. The authors noted that their results pointed to a magnetic-field modulated reverse intersystem crossing (RISC) between the triplet and singlet exciplexes but no model was provided except to say that the magnitude of the effect was inconsistent with the hyperfine mechanisms’s expectations.\(^{44}\)

The first detailed account of the exceptionally large experimental MEL and MC with a corresponding theory\(^{47}\) used a coevaporated donor-acceptor blend that had been earlier used in investigations of TADF at zero field.\(^{32}\) Device conditioning has been known to increase MFEs for some time\(^{57-62}\) but this work was the first to use the procedure on TADF materials. Unconditioned devices (pristine) displayed in Fig. 12(b) a MEL of about 20% at room temperature (in constant current mode) in a coevaporated m-MTDATA/3TPYMB(1:3) blend which is smaller than found by Basel \textit{et al.} in a different material combination.\(^{51}\) Under the particular conditioning procedure which can be found in Ref. 47, the MEL increased to 40% [Fig. 12(d)]. The same samples under constant voltage operation display dramatically larger responses: 60% and 1200% for pristine and conditioned devices,
Fig. 12. MEL measurements in a coevaporated $m$-MTDATA/3TPYMB(1:3) blend. (a), (b) pristine devices. (c), (d) conditioned devices. Experiments were performed in either the constant voltage (a), (c) or constant current (b), (d) modes. Taken from Ref. 47.

respectively. The large amplification is understood to be the result of the large nonlinearity of the I-V and EL-V curves,\textsuperscript{47} which is indicative of the increase in traps present from the conditioning process.\textsuperscript{63,64} An implication is that large MFEs in a constant voltage setting are much more sensitive to trap creation. Even so-called pristine devices still exhibited highly nonlinear EL-V curves which suggests that traps are unavoidable at present. Moreover reports of large MFEs may be misconstrued in terms of the underlying spin mixing mechanism instead of as a result of a highly nonlinear I-V or EL-V curve.
A quantitative model, based on the stochastic Liouville equation, was put forth that considered the spin mixing to be within the exciplex levels and to be dominated by difference in the $g$-factor. From this analysis the hyperfine interaction was deduced to yield observations contrary to their measurements (e.g. opposite sign of MEL and narrower widths). The model, as described in Section 3.1.2, produces an MEL width proportional to $\sqrt{k_D k_S/\delta g}$ where $k_D$ is the dissociation rate of the exciplexes and $k_S$ is the rate of fluorescence and $k_S \gg k_D \gg k_T$ where $k_T$ is the rate of phosphorescence. The model implicitly assumes that exciplexes are created from free polarons and not polaron pairs. Temperature dependence is accounted for by an exciplex generation matrix that preferentially places triplets in excited states resonant with $S_1$ as temperatures increase.

Shortly after Ref. 47, previous experimental work\(^{27}\) was extended in Ref. 52. The maximum MEL increased to near 160%, and the MEL and linewidth versus temperature were measured. A model of the $\delta g$ mechanism was suggested in which

$$\text{MEL} \sim \frac{1}{1 + (B/\Delta B)^2}, \quad (37)$$

where $\Delta B = h/(2\mu_B \delta g \tau)$ is the MEL width; $\tau$ is the lifetime of the electron-hole pair. The authors concluded that the large MEL widths ruled out hyperfine interactions and instead scaled with the lifetime $\tau$ in their model. Thus these results are consistent with Ref. 47.

In addition a comparison of different donor-acceptor combinations was conducted.\(^{52}\) With a single donor type, $m$-MTDATA, the acceptor was varied among the following options: 3TPYMB, Alq$_3$, PPT, TPBi, and PBD. The assumption was that different donor-acceptor combinations would have different singlet-triplet energy differences which would alter the magnetic-field modulated RISC. By measuring temperature dependence of the MEL, they extracted the activation energy, $E_a$, believed to correspond to the singlet-triplet energy gap. Ref. 52 noted that although $\delta g$ could only spin mix $S$ and $T_0$ states, spin lattice relaxation could convert $T_\pm$ to $T_0$ and so could therefore indirectly contribute to the RISC.
6. Fringe Field Effects in TADF Materials

As seen above, spin mixing driven by the δg mechanism only effectively mixes one of the three triplet eigenstates ($T_0$) with the singlet, leading to an anticipated efficiency improvement of 100%. The remaining two triplet eigenstates, $T_+$ and $T_-$, are not efficiently harvested into the singlet channel by the applied magnetic field. This limitation can be overcome by using the fringe magnetic field from a nearby ferromagnetic film. Harvesting all three triplet eigenstates would enhance OLED emission by 300%. A magnetic field gradient can be generated by the remanent magnetization of patterned ferromagnetic films which will mix in the other two triplet eigenstates, $T_+$ and $T_-$. Ref. 49 predicts that even OLED active regions that are 100 nm away from the ferromagnetic film can achieve the maximal (factor of 4) enhancement of light emission.

Shown in Fig. 13(a) is a schematic diagram of the recombination of polaron pairs into excitons. As described previously in the theory of magnetoelectroluminescence (Sec. 3), the spin character of the precursors (singlet or triplet) influences the rate of exciton formation. For exciplexes [Fig. 13(b)], the spin-mixing of singlet/triplet exciplex populations changes the emission efficiency. Figures 13(c–e) shows patterned domain stripes of magnetic material, whose magnetization can be reoriented by applied magnetic fields. These magnetic domains then remain configured (through the remanent magnetization) when the applied magnetic fields are turned off. Through this reconfiguration of the magnetic domains, the spin mixing via fringe fields can be switched on and off without any remaining applied external magnetic field. The form of the fringe field interaction produces very large changes in the electroluminescence $\Delta EL/EL = (EL(ON) - EL(OFF))/EL(OFF) = 300\%$.

Two options for striped patterns are shown in Figs. 13(c,d) for a thin magnetic film, with thickness $t$, with striped domains that generate fringe fields in the organic layer. The stripes repeat every distance $a$ along the $x$-axis and the film extends far out into the $y$-direction to ±c. The domains can be fixed perpendicular to the stripes [Fig. 13(c)] with sufficiently large $a$ and by applying
a magnetic field to set the domains perpendicular to the stripes. Strong fringe fields appear in this orientation, so this configuration is defined to be ON. Figure 13(d) is the most energetically favorable configuration, and corresponds to negligible fringe fields if edge effects are unimportant. This magnetic state is defined OFF, and a switching figure of merit is thus $\Delta E_L / E_L$.

The magnetic scalar potential from a ferromagnet with magnetization $\mathbf{M}$, volume $V$, and surface $S$, [Fig. 13(c)] is

$$\Phi(R) = \sum_i \frac{1}{4\pi} M_{s,i} \int_{S_i} \frac{n_i \cdot M_i(r_i)}{|R - r_i|} dA_i,$$

(38)
where each domain is assumed to be uniformly magnetized and is denoted by an index \( i \). \( \mathbf{R} = (X,Y,Z) \) is the position outside the magnet, \( \mathbf{r} = (x,y,z) \) the position within the magnet, and the \( A_i \) are area elements of the magnet’s surface. \( \mathbf{H} = \mathbf{B}/\mu_0 \) outside a magnetized volume, so \( \mathbf{B} = -\mu_0 \nabla \Phi(\mathbf{R}) \) where \( \mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2 \). \( M_{s,i} \) and the length and width of \( S_i \) are assumed to be constant for all \( i \) in a given configuration of the magnet.

The magnetized domains are separated spatially by non-magnetic stripes [Fig. 13(e)]. Magnetic surface charge densities form on each domain wall and alternate between positive and negative magnetic charge. These surfaces are located at each \( x_i \) and have an area \( 2c(z_t - z_b) = 2ct \), where \( z_t \) and \( z_b \) are the top and bottom positions of the magnet. \( x = 0 \) is halfway in between two such oppositely “charged” plates (the negative plate lies at \( x = +a/2 \) and the positive plate at \( x = -a/2 \)). Each plate (or domain wall) is indexed by \( x_i = (i + \frac{1}{2})a \) with \( -i_{\text{max}} < i < i_{\text{max}} - 1 \). The \( x \)-edge length is thus \( L_x = (2i_{\text{max}} - 1)a \). An approximation for infinite stripes (i.e. \( c \to \infty \)) that \( t \ll a, Z \), allows for simplified expressions for the fringe fields by expanding each term in small \( t \):

\[
\mathbf{B}_{\text{FF}}(\mathbf{R}) = -\frac{\mu_0}{4\pi} M_s \frac{4\pi t}{a} \left\{ \begin{array}{c}
- \cos \left( \frac{2\pi x}{a} \right) \cosh \left( \frac{2\pi Z}{a} \right), 0, \sin \left( \frac{2\pi x}{a} \right) \sinh \left( \frac{2\pi Z}{a} \right) \\
\cos \left( \frac{2\pi x}{a} \right) + \cosh \left( \frac{2\pi Z}{a} \right) \end{array} \right\}.
\]

Figure 13(e) shows the direction of the fringe fields above the magnetic domains in the \( x - z \) plane.

For the calculation of a figure of merit, Eq. (15) is solved in steady state with \( \mathbf{B}_{\text{FF}}(\mathbf{r}_1) \) calculated in the organic layer from Eq. (39). \( \mathbf{r}_1 \) is selected randomly within a box of height 30 nm, positioned at \( Z = Z_{\text{min}} \) above the magnet. The lateral size of the box is equal to the magnetic film’s lateral size. The current path is along the \( \hat{z} \) direction, so the average carrier hop occurs in the \( z \)-direction and \( \mathbf{B}_{\text{FF}}(\mathbf{r}_2) = \mathbf{B}_{\text{FF}}(\{x_1, y_1, z_1 + d\}) \), where \( d = 1 \text{ nm} \) is the hopping length. After determining the density matrix \( \rho \), the fluorescent EL is determined from \( \text{EL} \propto k_S \text{Tr} P_S \rho \).
Fig. 14. Change in EL versus average fringe field gradient and height above magnets in the absence of hyperfine fields. For the exciplex curves: $k_S = 3 \times 10^{-3} \text{ns}^{-1}$, $k_T = 0$, and each curve is labeled by the choice of $k_D$ (in ns$^{-1}$). The exciton curves are labeled by their values of $k_S$ (in ns$^{-1}$); other values used are $k_T = 2k_S$. We find $k_D$ has negligible effect on exciton responses and so it is taken to be zero. We specify the patterned FM to be permalloy with $M_s = 8 \times 10^5 \text{A/m}$, $t = 20 \text{nm}$, and $a = 160 \text{nm}$. From Ref. 49.

Figure 14 shows the figure of merit $\Delta \text{EL/EL}$ in a simplified model including only the fringe field ($\mathcal{H}_{\text{HF}} = 0$) within both the exciton and exciplex pictures. Beginning far above the magnet, and thus far from the fringe fields, the lack of a substantial fringe field gradient produces no spin mixing or change in electroluminescence. As the fringe field gradient is increased by reducing the height above the magnets, $Z_{\text{min}}$, the figure of merit plateaus at 100%. The reason for this plateau is reminiscent of the $\delta g$ mechanism for which all $T_0$ states may upconvert to $S$ states, doubling the electroluminescence. For $k_D$ large enough to prohibit further mixing the effect saturates. Thus these curves shift left as $k_D$ is increased. As the gradient increases further, and for sufficiently small dissociation, the figure of merit approaches 300%. This indicates that now all triplet exciplexes are spin mixing to singlet exciplexes and are recombining as singlets. Spin-selective rates for excitons vary little, contrary to what occurs with exciplexes, so the figure of merit is much smaller. We assume $k_S \ll k_T$.66
Fig. 15. Change in EL versus average fringe field gradient and height above magnets in the presence of hyperfine fields. Exciplexes (red): $k_S = 3 \times 10^{-3} \text{ns}^{-1}$, $k_T = 0$, $k_D = 10^{-6} \text{ns}^{-1}$. Excitons (blue): $k_S = 6 \times 10^{-4} \text{ns}^{-1}$, $k_T = 12 \times 10^{-1} \text{ns}^{-1}$, $k_D = 0$. $\Delta_{hf}$ is the width of the gaussian distribution from which the fields $B_{HF}$ are sampled when calculating the average figure of merit. The thickness of the organic layer is taken to be 10 nm. Calculations for shorter heights are not displayed as the condition $t << Z_{min}$ is not met for Eq. (39) and thus the results would not be valid. From Ref. 49.

If $k_S \gtrsim k_T$, the excitonic $\Delta\text{EL}/\text{EL}$ changes sign but still does not reach the magnitude seen for exciplexes.

When hyperfine interactions are included as well the figure of merit is modified from the results in Fig. 14. The changes are shown in Fig. 15. High above the magnets, where the fringe field is small, the figure of merit is zero. The fringe field in Fig. 15 acts like an external magnetic field influencing the usual (hyperfine-based) magnetoelectroluminescence for spin pairs. This picture is supported by the sign of the figures of merit which are opposite to those in Fig. 14.44,47 Even though hyperfine mixing is dominating the response, so plateaus in the figure of merit are not apparent and the magnitude is smaller, we see that the fringe fields still act as an ON/OFF switch.

The influence of the fringe fields within the Hamiltonian description is similar to the influence of the $\delta g$ mechanism of Sec. 3.1, but because the fringe field gradient is not necessarily aligned with the fringe field, the precessional mechanism is more efficient in converting triplet to singlets, and thereby increasing radiation more than in
Sec. 3.1 (to 300% instead of 100%). Conditioned devices governed by the $\delta g$ mechanism yield an MEL up to 4000% under constant-voltage operation, but only 40% for constant current (which is the mode assumed in our theory).\textsuperscript{47} Thus the larger constant-current MEL with fringe fields will lead to a corresponding larger than 4000% constant-voltage MEL in conditioned devices.

7. Conclusion

Chemists have explored photo-magnetic field effects on reactions for some time now; their most spectacular manifestation may be the role played in avian navigation mechanisms.\textsuperscript{11,12,67} Perhaps it is not surprising that such effects would prove to be influential in organic devices that emit light, however their importance in materials and devices that are of high efficiency, and their promise to potentially improve the light emitting efficiency of OLEDs, is gratifying to those looking for substantial quantum coherent effects at room temperature in electronic materials.

The discovery of very large magnetic field effects in exciplex emission provides an elegant example of a scenario in which the mathematical description of a new physical situation (exciplex emission, as indicated in our Table I) is considerably simpler, and with much more dramatic magnetic field effects, than in the original materials and excitations in which magnetic field effects were discovered (exciton emission). Analytic solutions of the magneto-electroluminescence are possible for the $\delta g$ mechanism for exciplex emission, and the maximum magnetic field effect is 100% in constant-current measurements. When the presence of fringe fields from inhomogeneous magnetic materials is included, which could provide an avenue to integrate magnetic memories with organic devices without electrical contacts between them, the maximum magnetic field effects are 300%!

Little discussion has been presented here regarding electrical transport to and from the donor-acceptor pair of relevance. Similar features should emerge in transport and in other forms of chemical reaction under the right conditions. In addition there is little fundamentally limiting the size of the regions that emit and respond
to these magnetic fields, since the dynamics considered here is essentially entirely within the donor-acceptor molecule complex.

This material is based on work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-SC0014336.

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