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Harvesting Emission in White Organic Light Emitting Devices

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1. Introduction

The current use of lighting in buildings and streets accounts for a significant percentage of the electricity consumed in the world at present and nearly 40% of that is consumed by inefficient thermoluminescent incandescent lamps, only about 15 lm/W. This has created interest in investigating more efficient electroluminescent sources of white light for use in domestic, industrial and street lighting. The total light output efficiency η_{out} of an electroluminescent lighting device depends on the internal quantum efficiency η_{int} and the photon out-coupling efficiency η_{ph} as [1]:

$$\eta_{out} = \eta_{int}\eta_{ph}, \quad (1)$$

where η_{int} is the ratio of number of radiative recombinations to the number of electrically injected electrons and holes from opposite electrodes of the device and it is given by:

$$\eta_{int} = \gamma\eta_{ex}. \quad (2)$$

Here γ is the ratio of number of electrons to that of holes, or vice versa, injected from the opposite electrodes of a device so that $\gamma \leq 1$ is maintained. η_{ex} is the fraction of the injected electron (e) and hole (h) pairs that recombine radiatively due to their Coulomb interaction.

$\eta_{ph} \approx \frac{1}{2n^2}$, where n is the index of refraction of the substrate through which the light comes out. In the case of a glass substrate with $n = 1.5$, $\eta_{ph} \approx 20\%$.

The schematic of a very simple electroluminescent device can be envisaged as a single thin film of an electroluminescent layer sandwiched between anode and cathode electrodes, as

shown in Fig. 1. In this case the anode is made of a transparent conducting oxide (usually indium tin oxide (ITO) and cathode is a metal, usually Al, Ca, Ag, etc). If the electroluminescent layer is of any direct band gap inorganic semiconductor, for example, based on GaAs and InP, then the injected electrons and holes from the cathode and anode, respectively, remain free electron and hole pairs and recombine radiatively by emitting light. In inorganic semiconductors, the static dielectric constant is relatively high (12.9 for GaAs and 12.5 for InP) which to a relative extent prevents the injected free charge carriers from forming bound hydrogenic excited states, called excitons. This is easy to understand as the attractive Coulomb potential energy between e and h is given by:

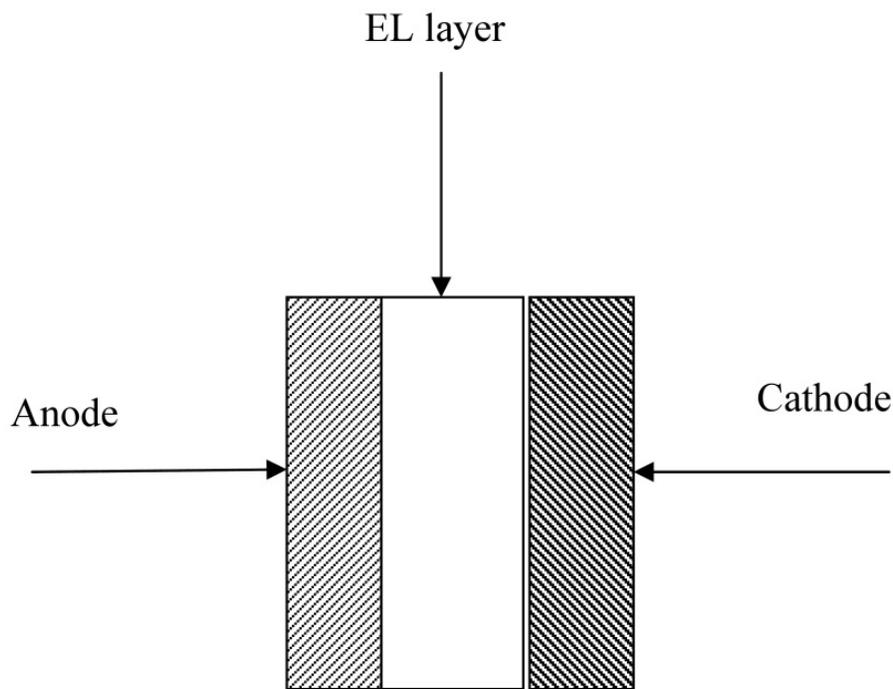


Figure 1. Schematic design of a single layered electroluminescent (EL) device sandwiched between anode and cathode electrodes.

$$E_p = -\frac{\kappa e^2}{\epsilon r}, \quad (3)$$

where $\kappa = (4\pi\epsilon_0)^{-1} = 8.9877 \times 10^9$, e is the electronic charge, ϵ is the static dielectric constant and r is the average separation between the injected electrons and holes. According to Eq. (3), materials with larger ϵ will have reduced binding energy (E_B) between the injected electrons and holes and hence they remain free charge carriers. The binding energy is equal to the magnitude of E_p ($E_B = |E_p|$) in Eq. (3).

In contrast organic semiconductors, both of small molecules and polymers, have lower dielectric constant ($\epsilon \approx 3$) which enhances the binding energy about four times larger than that in inorganic materials. Such a large binding energy between electrons and holes enables them to form excitons immediately after their injection from the opposite electrodes. On one

hand, the formation of excitons due to their Coulomb interaction assists their radiative recombination leading to electroluminescence. On the other hand, excitons can be formed in two spin configurations, singlet and triplet and this complicates the mechanism of radiative recombination because the recombination of singlet excitons is spin allowed but that of triplet excitons is spin forbidden. The singlet and triplet exciton configurations are shown in Fig. 2 and accordingly the probability of forming singlet and triplet excitons may be in the ratio of one to three (1:3). If the triplet excitons cannot recombine due to forbidden spin configuration, then the light emission can occur only through singlet excitons and that means internal quantum efficiency η_{int} can be only about 25%, and 75% of the injected electron-hole pairs will be lost through the non-radiative recombination due to the formation of triplet excitons. This limits the light-out efficiency $\eta_{out} = 0.25 \times 0.2 = 0.05 = 5\%$ according to Eq. (1).

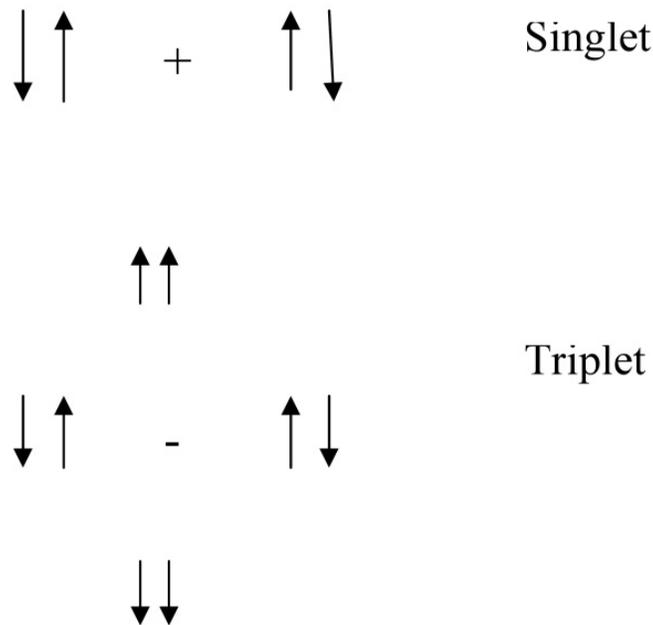


Figure 2. Spin configurations of electron and hole pairs in forming an exciton. Pairs of arrows represent pairs of electron and hole. The upper combination of spin configurations represents the single possibility for formation of a singlet exciton and lower three spin configurations represent the three possibilities for formation of a triplet exciton.

However, Cao *et al.* have found that the ratio of quantum efficiencies of EL with respect to PL in a substituted PPV-based LED can reach as high as 50% [2]. This higher quantum internal efficiency is attributed to larger cross section for an electron-hole pair to form a singlet exciton than that to form a triplet exciton [3] as explained below. If one denotes the cross section of the formation of a singlet exciton by σ_S and that of a triplet by σ_T then by assuming that all pairs of injected e and h form excitons, the internal quantum efficiency can be expressed in terms of cross sections as $\eta_{ex} = \frac{\sigma_S}{\sigma_S + 3\sigma_T}$. Thus, for $\sigma_S = \sigma_T$ one gets

$\eta_{ex} = 0.25$ (or 25%), for $\sigma_S = 3\sigma_T$, $\eta_{ex} = 0.5$ (50%) and for $\sigma_T = 0$, $\eta_{ex} = 1$ (100%). This suggests that if one can minimise the cross section of the formation of triplet excitons one can maximise the internal quantum efficiency in OLEDs. However, for modifying the cross sections one has to know the material parameters on which these cross sections depend and then one has to manipulate those parameters to minimise the triplet cross section. This approach has not been applied yet probably because the dependence of cross sections on the material parameters has not been well studied. The other approach of increasing η_{ex} to 100% is by harvesting the radiative emissions from all triplet excitons as well as has been achieved by Adachi et al. [1]. The mechanism of this approach and process will be presented in detail here.

Thus, as the formation of triplet excitons is more probable than singlet, it is very desirable to capture the full emission from triplet excitons in OLEDs. It may be noted that the mechanisms of singlet and triplet emissions are different because of their different spin configurations and therefore the emission from singlet excitons is known as electrofluorescence and that from triplet excitons as electrophosphorescence in analogy with the terms used in photoluminescence. The description presented above may raise a question in your mind why then one should make any effort in organic solids/polymers for fabricating light emitting devices if the emission from triplet excitons cannot be harvested. This is because OLEDs have the potential of being produced by one of the very cost effective chemical technologies.

In addition, by harvesting emissions from both singlet and triplet excitons not only the 100% internal quantum efficiency (η_{int}) can be achieved but also the white light emission can be achieved by incorporating fluorescent blue emitters (emission from singlet excitons) combined with phosphorescent green and red emitters (emission from triplet excitons) in the electroluminescent layer of OLEDs. Materials from which singlet emission can be harvested are called fluorescent or electro-fluorescent materials and those from which triplet emission is available are called phosphorescent or electro-phosphorescent materials. An OLED that can emit white light is called white OLED (WOLED) actually it is an organic white light emitting device (OWLED). A successful cost effective technological development of WOLEDs is going to provide a huge socio economic benefit to mankind by providing brighter and cheaper lighting. WOLEDs show promise to have a major share in the future ambient lighting due to their very favourable properties such as homogenous large-area emission, good colour rendering, and potential realization on flexible substrates. This is expected to open new ways in lighting design such as light emitting ceilings, curtains or luminous objects of almost any shape [4-5]. Therefore, much research efforts are continued in developing more cost effective and efficient white organic light emitting devices (WOLEDs) [4,6-7].

The performance of a WOLED can be optimised by finding optimum emitting materials, manipulating the charge carrier balances and location of the recombination zone and energy transfer. The first WOLED fabricated [6] had a single poly (N-vinylcarbazole) emission layer doped with three fluorescent dyes. To achieve higher power efficiency, a combined use of

blue fluorescent and green and red phosphorescent emitters in WOLEDs has been made recently [4,7]. This concept is based on the coincidence of a physical phenomenon of formation a singlet spin configuration with probability 25% and triplet with 75% between an electron and hole injected from the opposite electrodes of a device with that of a natural phenomenon that white light consists 25% of blue light and 75% of red and green lights. Thus, the combination of fluorescent (blue singlet emission) and phosphorescent (red and green or orange triplet emission) emitters is capable of reaching 100% internal quantum efficiency of white light emission by harvesting 25% singlet emission and 75% triplet emission. Although by trial and error experimental techniques on WOLEDs the triplet radiative recombination is activated by a heavy metal atom compound (phosphor) that enhances the spin-orbit interaction and hence triplet radiative recombination, the mechanism has not been fully understood theoretically until recently [8]. This is because the well known spin-orbit interaction is a stationary operator that cannot cause transitions[8-9].

In this chapter, the radiative recombination of both singlet and triplet excitons in organic solids/polymers is reviewed. Rates of spontaneous emission from both singlet and triplet excitons are calculated in several phosphorescent materials by using the recently invented new time-dependent exciton-spin-orbit-photon interaction operator [8] and found to agree quite well with the experimental results.

2. Emission from singlet excitons

Let us consider an excited pair of electron and hole created such that the electron (e) is excited in the lowest unoccupied molecular orbital (LUMO) and hole (h) in the highest occupied molecular orbital (HOMO) of organic layer sandwiched between two electrodes, and then they recombine radiatively by emitting a photon. The interaction operator between a pair of excited e and h and radiation can be written as:

$$\hat{H}_{xp} = -\left(\frac{e}{m_e^*} \mathbf{p}_e - \frac{e}{m_h^*} \mathbf{p}_h\right) \cdot \mathbf{A}, \quad (4)$$

where m_e^* and \mathbf{p}_e and m_h^* and \mathbf{p}_h are the effective masses and linear momenta of the excited electron and hole, respectively, and \mathbf{A} is the vector potential given by:

$$\mathbf{A} = \sum_{\lambda} \left(\frac{\hbar}{2\varepsilon_0 n^2 V \omega_{\lambda}} \right)^{1/2} \left[c_{\lambda}^+ \hat{\varepsilon}_{\lambda} e^{-i\omega_{\lambda} t} + c.c. \right], \quad (5)$$

where n is the refractive index, V is the illuminated volume of the material, ω_{λ} is the frequency and c_{λ}^+ is the creation operator of a photon in a mode λ , $\hat{\varepsilon}_{\lambda}$ is the unit polarization vector of photons and *c.c.* denotes complex conjugate of the first term. The second term of \mathbf{A} , which is the complex conjugate of the first term, corresponds to the absorption and will not be considered here onward. It may be noted that in organic solids

and polymers the effective masses of charge carriers are approximated by the free electron mass m_e , i.e., $m_e^* = m_h^* = m_e$.

Using the centre of mass, $\mathbf{R}_x = \frac{m_e^* \mathbf{r}_e + m_h^* \mathbf{r}_h}{M}$ and relative $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$ coordinate transformations, the interaction operator \hat{H}_{xp} [Eq. (4)] can be transformed into [10-11]:

$$\hat{H}_{xp} = -\frac{e}{\mu_x} \mathbf{A} \cdot \mathbf{p}, \quad (6)$$

where $\mathbf{p} = -i\hbar\nabla_r$ is the linear momentum associated with the relative motion between e and h and μ_x is their reduced mass ($\mu_x^{-1} = m_e^{*-1} + m_h^{*-1} = 2m_e^{-1} \Rightarrow \mu_x = 0.5m_e$ in organics). The operator in Eq. (6) does not depend on the centre of mass motion of e and h. Therefore, this operator [Eq. (6)] is the same for the exciton-photon interaction or a pair of e and h and photon interaction.

The field operator of an electron in LUMO can be written as:

$$|LUMO\rangle = \sum_{\sigma_e} |\Psi_{LUMO}\rangle a_{LUMO}(\sigma_e), \quad (7)$$

where $\Psi_{LUMO}(\mathbf{r}_e)$ is the molecular orbital wave function of an electron excited in the LUMO, \mathbf{r}_e is the position coordinate of the electron and $a_{LUMO}(\sigma)$ is the annihilation operator of an electron with spin σ_e .

Likewise the field operator of a hole excited in HOMO can be written as:

$$|HOMO\rangle = \sum_{\sigma_h} |\Psi_{HOMO}\rangle d_{HOMO}(\sigma_h), \quad d_{HOMO}(\sigma_h) = a_{HOMO}^+(-\sigma_h), \quad (8)$$

Using Eqs. (5), (7) and (8), the operator \hat{H}_{xp} [Eq. (6)] of interaction between an excited e-h pair and a photon can be written in the second quantized form as:

$$\hat{H}_{xp} = -\frac{e}{\mu_x} \sum_{\lambda, \sigma_e, \sigma_h} \left(\frac{\hbar}{2\epsilon_0 n^2 V \omega_\lambda} \right)^{1/2} Q_{LUMO, HOMO} c_\lambda^+, \quad (9)$$

where

$$Q_{LUMO, HOMO} = \langle \Psi_{LUMO} | \hat{\epsilon}_\lambda \cdot \mathbf{p} | \Psi_{HOMO} \rangle a_{LUMO}(\sigma_e) d_{HOMO}(\sigma_h), \quad (10)$$

We now consider a transition from an initial state $|i\rangle$ to a final state $|f\rangle$. The initial state is assumed to have one singlet exciton created by exciting an electron in LUMO and a hole in HOMO. The spin configurations for singlet and triplet excitons used here are given [8,12] as:

$$\begin{aligned} & \frac{1}{\sqrt{2}}[a_e(+1/2)d_g(-1/2) + a_e(-1/2)d_g(+1/2)] = \\ & \frac{1}{\sqrt{2}}[a_e(+1/2)a_g^+(+1/2) + a_e(-1/2)a_g^+(-1/2)] \end{aligned} \quad (11)$$

for singlets and

$$\begin{aligned} & a_e(+1/2)d_g(+1/2) = a_e(+1/2)a_g^+(-1/2) \quad (a) \\ & \frac{1}{\sqrt{2}}[a_e(+1/2)d_g(-1/2) - a_e(-1/2)d_g(+1/2)] = \quad (b) \\ & \frac{1}{\sqrt{2}}[a_e(+1/2)a_g^+(+1/2) - a_e(-1/2)a_g^+(-1/2)] \\ & a_e(-1/2)d_g(-1/2) = a_e(-1/2)a_g^+(+1/2) \quad (c) \end{aligned} \quad (12)$$

for triplets. We assume that there are no photons in the initial state and the final state has no excitons but only a photon in a λ mode. The transition matrix element is then obtained for singlet excitons as [10,11]:

$$\langle f | \hat{H}_{xp} | i \rangle = -\frac{e}{\mu_x} \sum_{\lambda} \left(\frac{\hbar}{2\varepsilon_0 n^2 V \omega_{\lambda}} \right)^{1/2} p_{LUMO,HOMO}, \quad (13)$$

where

$$p_{LUMO,HOMO} = \langle \Psi_{LUMO} | \hat{\varepsilon}_{\lambda} \cdot \mathbf{p} | \Psi_{HOMO} \rangle = i\omega\mu_x |r_{e-h}|. \quad (14)$$

Here the energy difference between the LUMO and HOMO levels is given by $\hbar\omega = E_{LUMO} - E_{HOMO}$ and $|r_{e-h}|$ is the mean separation between the excited electron and hole. It may be noted that for triplet excitons the transition matrix element vanishes. This can be easily verified using Eqs. (9) and (12). Using Fermi's golden rule for such a two level system and the transition matrix element [Eq. (13)], the rate of spontaneous emission, R_{sp12} , is obtained as [11]:

$$R_{sp12} = \frac{4\kappa e^2 \sqrt{\varepsilon} \omega^3 |r_{e-h}|^2}{3\hbar c^3}, \quad (15)$$

where $\varepsilon = n^2$ is the static dielectric constant and hole and $\kappa = 1/(4\pi\varepsilon_0)$. For a quantitative evaluation $|r_{e-h}|$ one should evaluate the integral in Eq. (14) using the LUMO and HOMO molecular orbitals. However, for excitons $|r_{e-h}|$ can be replaced by their excitonic Bohr radius as $|r_{e-h}| = a_x^S / \varepsilon$, a_x^S being the singlet excitonic Bohr radius and given by [10,12]:

$$a_x^S = \frac{\alpha^2}{(\alpha - 1)^2} a_x^T \quad \text{where} \quad a_x^T = \frac{\mu\varepsilon}{\mu_x} a_0, \quad (16)$$

where a_x^T is the excitonic Bohr radius of a triplet exciton, $a_0 = 0.0529$ nm is the Bohr radius, and μ reduced mass of electron in hydrogen atom which is used here as equal to the free electron mass. The parameter α depends on the energy difference, ΔE_x , between singlet and triplet exciton states as [12]:

$$\alpha = \left[1 - \sqrt{1 - \frac{\Delta E_x}{C_M}} \right]^{-1} \quad \text{and} \quad C_M = \frac{\mu_x e^4 \kappa^2}{2\hbar^2 \epsilon^2} \quad (17)$$

In organic solids, ΔE_x is estimated to be 0.7 eV [9,13] which gives $\alpha = 1.38$ with $\epsilon = 3$ and the triplet exciton Bohr radius as $a_x^T = 6a_0$. According to Eq. (16) then we get the singlet exciton Bohr radius as $a_x^S \approx 79a_0$ and $|r_{e-h}| = 26.3 a_0$. As an example, 4,40-bis(9-ethyl-3-carbazovinylylene)-1,10-biphenyl [BCzVBi] used as a fluorophor in WOLEDs [4,7] has a singlet energy of 2.75 eV and corresponds to $\omega = 4.21 \times 10^{15}$ Hz. Using these in Eq. (15), one finds the rate of spontaneous emission from singlet excitons in BCzVBi is $R_{sp12} = 2.7 \times 10^{10} \text{s}^{-1}$ and the radiative lifetime $\tau_R = R_{sp12}^{-1} = 3.7 \times 10^{-11}$ s. This radiative lifetime may be considered to be much shorter than the singlet lifetime usually found in the ns range. The discrepancy may be attributed to the approximations involved and to the fact that the rate depends on third power of the frequency of emitted light (ω^3), which is quite high in this case.

3. Emission from triplet excitons

As recombination of a triplet exciton state to the ground state is spin forbidden, it cannot occur unless either the triplet goes through an intersystem crossing to a singlet or a source of flipping the spin is introduced to make such a radiative recombination possible. Unlike inorganic solids, most organic solids and polymers have significant exchange energy between singlet and triplet excitons states. Therefore the mechanism of intersystem crossing may not be very efficient without doping the solids with another material of lower singlet energy state. This is possible and usually the host material is doped with a fluorescent material but some loss of energy is inevitable due to the difference in energy [4]. A more efficient way of harvesting triplet is to dope the host material with phosphorescent compounds containing heavy metal atoms, like platinum (Pt), palladium (Pd) or iridium (Ir) [1]. Here again the energy matching needs to be carefully examined otherwise an energy loss will occur. Thus, in the fabrication of a WOLED, the host polymer is doped with a fluorophore to emit the blue emission from singlet excitons and two phosphorescent compounds to emit green and red from the triplet radiative recombination [4,7]. A most efficient such combination is the host polymer being doped with a blue fluorophore 4,4'-bis(9-ethyl-3-carbazovinylylene)-1,1'-biphenyl (BCzVBi) 12 in a region separate from the phosphorescent dopants, which are fac-tris (2-phenylpyridine) iridium(Ir(ppy)₃) for emitting green and iridium(III) bis(2-phenyl quinolyl-N,C20) acetylacetonate (PDIr) for

emitting red [4]. In some cases an orange phosphorescent dopant is used in place of red and green. It is commonly well established that the transfer of singlet excitons to blue fluorophore occurs efficiently due to the Förster transfer and that of triplet excitons to phosphorescent dopants due to Dexter or diffusive transfer. However, after that how the radiative recombination occurs by the enhanced spin-orbit interaction due to the introduction of heavy metal atoms is not thoroughly explored. The problem is that the well known expression for an electron spin-orbit interaction in an atom is given by:

$$\hat{H}_{so} = \frac{Ze^2}{2m_e^2 c^2 r^3} \mathbf{s} \cdot \mathbf{L}, \quad (18)$$

where Z is the atomic number and r is the distance of an electron from the nucleus. \mathbf{s} and \mathbf{L} are the spin and orbital angular momentum of the electron, respectively. It is obvious that the spin-orbit interaction, \hat{H}_{so} in eq. (18) is zero for $\mathbf{s} = \mathbf{L} = \mathbf{0}$, i.e. for all s -state orbitals with $l = 0$ and also for singlet excitations ($\mathbf{s} = \mathbf{0}$). It is only non-zero for p - type or higher state orbitals. As the interaction in Eq. (18) is derived for a single electron in an atom, it cannot be applied for excitons which consist of a pair of electron and hole. Therefore, it cannot contribute to the radiative recombination of a triplet exciton in a semiconductor where both the singlet and triplet spin configurations arise from the first excited s -state with $n = 1$ and $l = 0$. However, the photoluminescence spectra from both singlet and triplet excitons in the first excited state have been observed in amorphous semiconductors [14-15] as well as in WOLEDs [1].

Furthermore, the interaction operator given in Eq. (18) is a stationary interaction operator, i.e., \mathbf{s} and \mathbf{L} are intrinsic properties of charge carriers (electrons and holes) and are always with them. These are present in all atoms all the time like the Coulomb interaction between electrons and nucleus. Such an interaction can give rise only to the stationary effects, like splitting the degeneracy of a triplet state but it cannot cause any transitions. As the splitting depends on the strength of the spin-orbit interaction, which increases with Z , the splitting usually increases with the atomic number of the constituting atoms. However, in solids its magnitude can usually be estimated only from the experimental data (see, e.g., [16]). To the author's knowledge any such splitting in semiconductors has not been calculated theoretically.

We have recently addressed the problem [8-9] of finding a new time-dependent exciton-spin-orbit-photon interaction operator as described below.

3.1. Electron-spin-orbit-photon interaction

We consider the case of an atom of atomic number Z excited to a triplet state. Instead of using the interaction operator given in Eq. (18), we start from the interaction of an electron of spin angular momentum \mathbf{s} , linear momentum \mathbf{p} moving under the influence of the electric field \mathbf{E} created by the nucleus as [17]:

$$\hat{H}_{so}^{at} = -\frac{eg}{2m_e^2c^2} \mathbf{s} \cdot \mathbf{p} \times \mathbf{E} \quad (19)$$

where g is the gyromagnetic ratio ($g = 2$), \mathbf{s} and \mathbf{p} are the spin angular and orbital momenta of the electron, respectively, and \mathbf{E} is the electric field experienced by the electron due to the nucleus. If we now shine light on the atom then the interaction operator in Eq. (19) changes to:

$$\hat{H}_{so}^{at} = -\frac{eg}{2m_e^2c^2} \mathbf{s} \cdot \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right) \times \left(-\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla V_n \right) + \frac{eg}{m_e c} \mathbf{s} \cdot \mathbf{H}, \quad (20)$$

where \mathbf{A} is the vector potential of photons as used in Eq. (5) but expressed in a different form here (see Eq. (21)), V_n is the scalar potential of the nucleus and $\mathbf{H} = \nabla \times \mathbf{A}$ is the magnetic field of the electromagnetic radiation. The interaction operator in Eq. (19) gets modified in Eq. (20) due to the interaction with the electromagnetic radiation, which changes the electron orbital momentum as well as the electric field and introduces interaction between the spin of electron and magnetic field of radiation.

Within the dipole approximation ($e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} \approx 1$), the vector potential is given by:

$$\mathbf{A} = \sum_{\lambda} A_0 \hat{\epsilon}_{\lambda} c_{\lambda}^{\dagger} e^{-i\omega_{\lambda} t} + c.c., \quad (21)$$

where $A_0 = \left[\frac{2\pi c^2 \hbar}{\epsilon_0 \omega_{\lambda} V} \right]^{1/2}$. The nuclear electric field $\mathbf{E} = -\nabla V_n$, where the scalar nuclear potential V_n is given by:

$$V_n = \frac{Zek}{r_e}, \quad \text{and} \quad \nabla V_n = -\frac{Zek}{r_e^3} \mathbf{r}_e \quad (22)$$

where \mathbf{r}_e is the position vector of the electron from the nucleus and $|\mathbf{r}_e| = r_e$. For $Z > 1$, the interaction between the excited electron and other valence electrons in the atom is considered to be negligible [18].

The interaction operator in Eq. (20) can be further simplified by noting that within the dipole approximation we get $\nabla \times \mathbf{A} = \mathbf{0}$, which makes the magnetic contribution vanish and also two other terms vanish because of the following:

$$\begin{aligned} \frac{e}{c^2} \mathbf{s} \cdot \left(\mathbf{A} \times \frac{\partial \mathbf{A}}{\partial t} \right) &= \mathbf{0} & (a) \\ \text{and} & & (23) \\ \frac{1}{c} \mathbf{s} \cdot \mathbf{p} \times \frac{\partial \mathbf{A}}{\partial t} &= -\frac{i\hbar}{c} \mathbf{s} \cdot \nabla \times \frac{\partial \mathbf{A}}{\partial t} = -\frac{i\hbar}{c} \mathbf{s} \cdot \frac{\partial}{\partial t} (\nabla \times \mathbf{A}) = \mathbf{0} & (b) \end{aligned}$$

Even otherwise, the contribution of the term in (23b) is expected to be small and therefore will not be considered here.

Substituting Eqs. (22) and (23) in Eq. (20) the interaction operator contains only the following two non-zero terms:

$$\hat{H}_{so}^{at} = -\frac{eg}{2m_e^2 c^2} \left(-\frac{Ze\kappa \mathbf{s} \cdot \mathbf{L}}{r_e^3} - \frac{e}{c} \mathbf{s} \cdot (\mathbf{A} \times \nabla V) \right), \quad (24)$$

where $\mathbf{L} = \mathbf{r}_e \times \mathbf{p}$ is the orbital angular momentum of electron. The first term of Eq. (24) is the usual stationary spin-orbit interaction operator as given in Eq. (18) and it is obtained in the absence of radiation. Its inclusion in the Hamiltonian as a perturbation can only split the degeneracy of a triplet state. As explained above, this term is a stationary operator and hence it cannot cause a transition. Only the last term, which depends on spin, radiation and time can be considered as the time-dependent perturbation operator and hence can cause transitions. Using Eqs. (21) and (22), the last term of Eq. (24), denoted by $\hat{H}_{so}^{at(t)}$, can be written for an atom or a two level system as:

$$\hat{H}_{so}^{at(t)} = -\frac{e^3 g Z \kappa}{2m_e^2 c^2 r_e^2} \sum_{\lambda} \left(\frac{2\pi \hbar}{\epsilon_0 \omega_{\lambda} V} \right)^{1/2} e^{-i\omega t} \mathbf{s} \cdot (\hat{\epsilon}_{\lambda} \times \hat{\mathbf{r}}_e) c_{\lambda}^+, \quad (25)$$

where $\hat{\mathbf{r}}_e = \frac{\mathbf{r}_e}{r_e}$ is a unit vector. For evaluating the triple scalar product of three vectors, without the loss of any generality we may assume that vectors $\hat{\epsilon}_{\lambda}$ and $\hat{\mathbf{r}}_e$ are in the xy-plane at an angle ϕ_{λ} , then we get $\hat{\epsilon}_{\lambda} \times \hat{\mathbf{r}}_e = \sin \phi_{\lambda} \hat{\eta}$, $\hat{\eta}$ being a unit vector perpendicular to the xy-plane. This gives $\mathbf{s} \cdot (\hat{\epsilon}_{\lambda} \times \hat{\mathbf{r}}_e) = \mathbf{s} \cdot \hat{\eta} \sin \phi_{\lambda} = s_z \sin \phi_{\lambda}$, which simplifies Eq. (25) as:

$$\hat{H}_{so}^{at(t)} = -\frac{e^3 g Z \kappa}{2m_e^2 c^2 r_e^2} \sum_{\lambda} \left(\frac{2\pi \hbar}{\epsilon_0 \omega_{\lambda} V} \right)^{1/2} e^{-i\omega t} \sin \phi_{\lambda} s_z c_{\lambda}^+. \quad (26)$$

For an atom, the field operator for an electron in the excited state and a hole in the ground state can be respectively written as:

$$\begin{aligned} |\hat{\psi}_e(r_e)\rangle &= \sum_{\sigma_e} \varphi_e(r_e, \sigma_e) a_e(\sigma_e), & (a) \\ \text{and} & & (27) \\ |\hat{\psi}_h(r_e)\rangle &= \sum_{\sigma_h} \varphi_g^*(r_e, \sigma_h) d_g(\sigma_h), \quad d_g(\sigma) = a_g^+(-\sigma) & (b) \end{aligned}$$

where $\varphi(r_e, \sigma)$ is the electron or hole wave functions as a product of orbital and spin functions corresponding to spin $\sigma = 1/2$ or $-1/2$, and $a_e(\sigma)$ and $d_g(\sigma)$ are the annihilation operators of an electron in the excited state and hole in the ground state, respectively. It may be noted that in an atom it is the same electron that is excited from the ground to the excited state therefore the same coordinate r_e is used for both the electron and hole in Eq. (27).

Using Eq. (27), the interaction operator in Eq. (26) can be expressed in second quantization as:

$$\hat{H}_{so}^{at(t)} = -\frac{e^3 g Z \kappa}{2m_e^2 c^2 r_e^2} \sum_{\lambda} \left(\frac{2\pi \hbar}{\epsilon_0 \omega_{\lambda} V} \right)^{1/2} e^{-i\omega t} \sin \phi_{\lambda} \langle \varphi_h(r_e) | r^{-2} | \varphi_e(r_e) \rangle \times \delta_{\sigma_e, -\sigma_h} s_z a_e(\sigma_e) d_g(\sigma_h) c_{\lambda}^+ \quad (28)$$

Using the property of the spin operator $s_z a_e(\pm \frac{1}{2}) = \pm \frac{1}{2} \hbar a_e(\pm \frac{1}{2})$ we find that only the integral from Eq. (12b) is non-zero and then the operator in Eq. (28) becomes:

$$\hat{H}_{so}^{at(t)} = -\frac{\hbar e^3 g Z \kappa}{4m_e^2 c^2} \sum_{\lambda} \left(\frac{2\pi \hbar}{\epsilon_0 \omega_{\lambda} V} \right)^{1/2} e^{-i\omega t} \sin \phi_{\lambda} [\langle \varphi_h(r_e) | r_e^{-2} | \varphi_e(r_e) \rangle \times \left[\frac{1}{\sqrt{2}} (a_e(+1/2) d_g(-1/2) + a_e(-1/2) d_g(+1/2)) \right] c_{\lambda}^+ \quad (29)$$

It may be noted that the operator s_z has flipped the triplet spin configuration to a singlet configuration and hence the recombination can now occur.

We now consider a transition from an initial state with a triplet excitation whose spin has been flipped by the spin-orbit interaction but it has no photons to a final state with no excitation (ground state) and one photon created in a mode λ . Within the occupation number representation, such initial $|i\rangle$ and final $|f\rangle$ states can be respectively written as:

$$|i\rangle = \frac{1}{\sqrt{2}} [a_e^+(+1/2) d_g^+(-1/2) + a_e^+(-1/2) d_g^+(+1/2)] |0\rangle |0_p\rangle, \quad (30)$$

$$|f\rangle = c_{\lambda}^+ |0\rangle |0_p\rangle, \quad (31)$$

where $|0\rangle$ and $|0_p\rangle$ represent the vacuum states of electrons (no excitations) and photons (no photons), respectively. Using Eqs. (29) - (31) and the usual anti-commutation rules for fermion and commutation rules for boson operators, the transition matrix element is obtained as:

$$\langle f | \hat{H}_{so}^{at(t)} | i \rangle = -\frac{\hbar e^3 g Z \kappa}{4m_e^2 c^2} \left(\frac{2\pi \hbar}{\epsilon_0 \omega_{\lambda} V} \right)^{1/2} e^{-i\omega_{\lambda} t} \sin \phi_{\lambda} \langle \varphi_h(r_e) | r_e^{-2} | \varphi_e(r_e) \rangle, \quad (32)$$

Using Fermi's golden rule and Eq. (32), the rate of spontaneous emission of a photon from the radiative recombination of a triplet excitation in an atom denoted by R_{sp}^{atom} (s^{-1}), is obtained as:

$$R_{sp}^{atom} = \frac{2\pi}{\hbar} \sum_{\lambda} |\langle f | \hat{H}_{so}^{at(t)} | i \rangle|^2 \delta(E_e - E_g - \hbar \omega_{\lambda}), \quad (33)$$

where the sum over λ represents summing over all photon modes and E_e and E_g are the energies of the excited and ground states. This can be evaluated as follows: Considering that a wave vector \mathbf{k} can be associated with every photon mode, one can write:

$$\sum_{\lambda} = \frac{2V}{(2\pi)^3} \int d^3\mathbf{k}, \quad \text{with} \quad k = \omega_{\lambda} / c, \quad k^2 dk = \frac{\omega_{\lambda}^2}{c^3 \hbar} d(\hbar\omega_{\lambda}) \quad \text{and} \quad \text{then} \quad \sum_{\lambda} = \frac{2V}{(2\pi)^3} \int d^3\mathbf{k} =$$

$$= \frac{2V}{(2\pi)^3} \int_0^{\hbar\omega_{12}} \int_0^{\pi} \int_0^{2\pi} \frac{\omega_{\lambda}^2}{c^2 \hbar} \sin\theta \sin^2\phi_{\lambda} d(\hbar\omega_{\lambda}) d\theta d\phi_{\lambda}. \quad \text{Using this we can replace the sum in Eq. (33) by}$$

a triple integration and then substituting $g = 2$ we get:

$$R_{sp}^{atom} = \frac{e^6 Z^2 \kappa^2 \hbar \omega_{12}}{2m_e^4 c^7 \epsilon_0 |r|^4}, \quad (34)$$

where $\hbar\omega_{12} = E_e - E_g$ and $|\langle \varphi_h(r_e) | r_e^{-2} | \varphi_e(r_e) \rangle|^2 = |r|^{-2}$ with $|r|$ being the average distance of an electron in the triplet excited state from the nucleus. It is to be noted that the rate of the spontaneous emission derived in Eq. (34) is very sensitive to the separation between the excited electron and nucleus, $|r|$, and the electronic mass but not so sensitive to the emitted photon energy. These properties are different from the rate of spontaneous emission from a singlet state derived in Eq. (15). The inverse of the rate of spontaneous emission gives the radiative lifetime τ_R [$(R_{sp}^{atom})^{-1} = \tau_R$], which can easily be calculated provided ω_{12} and r are known.

The rate of spontaneous emission obtained in Eq. (34) is derived within the two level approximation may be applied to organic solids and polymers [9] where excitation gets confined on individual molecules/monomers as Frenkel excitons and also referred to as molecular excitons [19]. Until the late seventies excitons in organic solids, like naphthalene, anthracene, etc., were regarded in this category. Furthermore, the concept that an exciton consists of an excited electron and hole pair was considered to be applicable only for excitons created in inorganic solids, known as Wannier excitons or Wannier-Mott excitons. These were also known as the large radii orbital excitons because of the small binding energy the separation between electron and hole is relatively larger than that in Frenkel excitons in organic solids. However, this distinction has blurred since the development of OLEDs where electrons and holes are injected from the opposite electrodes, as described above, and form Frenkel excitons. This proves the point that Frenkel excitons also consist of the excited electron and hole pairs but they indeed form a molecular excitations because of the small overlap between the intermolecular electronic wavefunctions.

Assuming that the Frenkel excitons are molecular excitons in organic solids/polymers, the above theory has been extended to organic solids [9] and the rate of spontaneous emission is obtained as:

$$R_{sp}^{mol} = \frac{e^6 Z^2 \kappa^2 \hbar \omega_{12}}{2m_e^4 c^7 \varepsilon^3 \varepsilon_0 |r|^4} \quad (35)$$

where ε is the static dielectric constant of the solid $|r|$ is the average separation between the electron and hole and $|r| = a_x^T / \varepsilon$, a_x^T being the excitonic Bohr radius of a triplet exciton given by $a_x^T = \frac{\mu \varepsilon}{\mu_x} a_0$ [8,12], $a_0 = 0.0529$ nm is the Bohr radius. Substituting this in equation (35), the rate of spontaneous emission from a triplet excitation in molecular semiconductors and polymers is obtained as:

$$R_{sp} = \frac{e^6 Z^2 \kappa^2 \varepsilon \hbar \omega_{12}}{2\mu_x^4 c^7 \varepsilon_0 a_x^4} \quad (36)$$

As the rate of spontaneous emission is proportional to Z^2 , it becomes very clear why the presence of heavy atoms enhances the rate of radiative emission of triplet excitons. The radiative lifetime of triplet excitons is calculated from the inverse of the rate in equation (36), $\tau_R = 1 / R_{sp}$.

The rate of spontaneous emission in equation (36) is used to calculate the triplet radiative rates in several organic molecular complexes, conjugated polymers containing platinum in the polymer chain and some organic crystals [9]. For all polymers considered from ref.[20], where the effective mass of charge carriers and excitonic Bohr radius are not known, it is assumed that $m_e^* = m_h^* = m_e$ giving $\mu_x = 0.5m_e$ and $\varepsilon = 3$, which give the triplet excitonic Bohr radius $a_x = \frac{m_e \varepsilon}{\mu_x} a_0 = 6a_0$. The first three polymers P₁, P₂ and P₃ are chosen from ref.

[20], where the rates of radiative recombination have been measured in many polymers containing platinum atoms. We can calculate the radiative rates for all the polymers studied in [20] but as they are all found to be of the same order of magnitude only the rates for the first three polymers are listed here. The triplet emission energy used in the calculation, and the calculated rate and the corresponding radiative lifetime are listed in table 1 along with the observed experimental rates and radiative lifetimes. For conjugated polymers incorporated with platinum atoms, the rates of radiative recombination in P₁, P₂ and P₃ are found to be of the order of 10^3 s^{-1} , which agrees very well with the experimental results [20]. In table 1 are also included the rate of spontaneous emission and radiative lifetime calculated for platinum porphyrin (PtOEP) used as a phosphorescent dye in organic electroluminescent devices [21] and phenyl-substituted poly (phenylene-vinylene) (PhPPV)[9]. From table 1, it is quite clear that the rate in equation (3) can be applied to most organic semiconductors and polymers because the calculated rates and radiative lifetimes agree very well with the experimental results.

Material	$\hbar\omega_{12}$ (eV)	R_{sp} (s ⁻¹) Eq. (3)	R^{exp} (s ⁻¹)	$\tau_R = 1 / R_{sp}$ (s)	τ^{exp} (s)
Benzene	3.66 [22]	0.63	-	1.6	4-7 [22]
Naphthalene	2.61 [22]	0.45	-	2.2	2.5 [22]
Anthracene	1.83 [22]	0.31	-	3.19	0.1 [22]
P1	2.40 [20]	5.5x10 ³	(6 ± 4)x10 ³ [23]	1.82x10 ⁻⁴	
P2	2.25 [20]	5.1x10 ³	(1.8 ± 0.9)x10 ³ [23]	1.96x10 ⁻⁴	
P3	2.05 [20]	4.6x10 ³	(1 ± 1)x10 ³ [23]	2.17x10 ⁻⁴	
Pt(OEP)	1.91[24]	4.9 x10 ³		2.03x10 ⁻⁴	7.00x10 ⁻⁴

Table 1. Assuming $m_e^* = m_h^* = m_e$, which gives $\mu_x = 0.5m_e$ and taking $\varepsilon = 3$, rates of spontaneous emission are calculated from equation (36) for a few molecular crystals, conjugated polymers and platinum porphyrin [Pt(OEP)]. Using these the triplet excitonic Bohr radius becomes $a_x = 6a_0$.

3.2. Exciton -spin-orbit-photon interaction

In the above section, it is shown that a time-dependent electron-photon-spin-orbit interaction operator does exist and it can be applied for triplet state transitions. The theory is also extended to Frenkel excitons or molecular excitons without considering them as consisting of electron and hole pairs. However, the formalism presented above is relevant to an excited electron in an atom/molecule which is not consistent with the situation occurring in a WOLED, where electrons and holes are injected from the opposite electrodes and they form excitons before their radiative recombination. Thus, for WOLEDs we need a time-dependent exciton-photon-spin-orbit interaction operator. For a pair of injected carriers in a solid with N atoms, an operator analogous to Eq. (19) and denoted by H_{so}^{sol} can be written as [9]:

$$\hat{H}_{so}^{sol} = -\frac{eg}{2\mu_x^2 c^2} \mathbf{s}_e \cdot (\mathbf{p}_e \times \sum_{n=1}^N \mathbf{E}_{ne}) + \frac{eg}{2\mu_x^2 c^2} \mathbf{s}_h \cdot (\mathbf{p}_h \times \sum_{n=1}^N \mathbf{E}_{nh}) \quad (37)$$

where μ_x is the reduced mass of exciton as described above. Other quantities with subscript e represent the electron and with subscript h represent the hole. In the presence of radiation, Eq. (37) becomes:

$$\begin{aligned} \hat{H}_{so}^{a-sem} = & -\frac{eg}{2\mu_x^2 c^2} \mathbf{s}_e \cdot (\mathbf{p}_e + \frac{e}{c} \mathbf{A}_e) \times \left(-\frac{1}{c} \frac{\partial \mathbf{A}_e}{\partial t} - \sum_{n=1}^N \nabla V_{ne} \right) \\ & + \frac{eg}{2\mu_x^2 c^2} \mathbf{s}_h \cdot (\mathbf{p}_h - \frac{e}{c} \mathbf{A}_h) \times \left(-\frac{1}{c} \frac{\partial \mathbf{A}_h}{\partial t} - \sum_{n=1}^N \nabla V_{nh} \right) \end{aligned} \quad (38)$$

where the zero magnetic contribution is neglected. In analogous with Eq. (24), one gets two non-zero terms for the electron and two for the hole as:

$$\begin{aligned} \hat{H}_{so}^{a-sem} = & -\frac{eg}{2\mu_x^2 c^2} \left(-\sum_{n=1}^N \frac{Z_n e \kappa \mathbf{s}_e \cdot \mathbf{L}_{en}}{\epsilon r_{en}^3} - \frac{e}{c} \mathbf{s}_e \cdot (\mathbf{A}_e \times \sum_{n=1}^N \nabla V_{ne}) \right) \\ & + \frac{eg}{2\mu_x^2 c^2} \left(-\sum_{n=1}^N \frac{Z_n e \kappa \mathbf{s}_h \cdot \mathbf{L}_{hn}}{\epsilon r_{hn}^3} + \frac{e}{c} \mathbf{s}_h \cdot (\mathbf{A}_h \times \sum_{n=1}^N \nabla V_{nh}) \right) \end{aligned} \quad (39)$$

Here Z_n is the atomic number of n^{th} atom and r_{en} and r_{hn} are, respectively, the electron and hole distances from their nuclear site n . s_{ez} and s_{hz} are the spin projections along the z -axis of the electron and hole, respectively, in an exciton. Other symbols have their usual meanings [9]. It may be pointed out here that the interaction operator as obtained in Eq. (26) is the same for a triplet exciton and an excited pair of electron and hole in a triplet spin configuration. Following the procedures applied in deriving Eq. (26) for a single electron, we get the time-dependent exciton-photon-spin-orbit interaction in a solid as [9]:

$$\begin{aligned} \hat{H}_{so}^{a-sem(t)} = & -\frac{e^3 g \kappa}{2\mu_x^2 \epsilon c^2} \sum_{\lambda, n} \left[\frac{Z_n}{r_{en}^2} \left(\frac{2\pi \hbar}{\epsilon_0 \epsilon \omega_\lambda V} \right)^{1/2} \sin \phi_{\lambda en} s_{ez} \right. \\ & \left. + \sum_{\lambda, n} \frac{Z_n}{r_{hn}^2} \left(\frac{2\pi \hbar}{\epsilon_0 \epsilon \omega_\lambda V} \right)^{1/2} \sin \phi_{\lambda hn} s_{hz} \right] e^{-i\omega_\lambda t} c_\lambda^+ \end{aligned} \quad (40)$$

Using the field operators in Eqs. (7) and (8) and Eq. (40), the time-dependent operator of exciton-photon-spin-orbit interaction is obtained in second quantisation as [9]:

$$\hat{H}_{so}^{(t)} \approx -\frac{e^3 g Z \kappa}{\mu_x^2 c^2 \epsilon r^2} \left(\frac{2\pi \hbar}{\epsilon_0 \epsilon V} \right)^{1/2} \sum_{\lambda} \sum_{\sigma_e, \sigma_h} \frac{\sin \lambda}{\sqrt{\omega_\lambda}} e^{-i\omega t} (s_{ez} + s_{hz}) a_e(\sigma_e) d_g(\sigma_h) \delta_{\sigma_e, \sigma_h} c_\lambda^+ \quad (41)$$

where r is the average separation between electron and hole in an exciton and it is approximated by:

$$\langle \text{HOMO} | r_{en}^{-2} | \text{LUMO} \rangle \approx \langle \text{HOMO} | r_{hn}^{-2} | \text{LUMO} \rangle \approx (r/2)^{-2}. \quad (42)$$

The other important approximation made in Eq. (41) is that the sum over sites n has disappeared. This is briefly because of the fact that the interaction operator depends on the atomic number Z_n and the inverse square of the distance between an electron and nucleus and hole and nucleus. Therefore only the heaviest and rearest atom will contribute most and the contribution of other atomic sites will be negligible. Using this approximation the summation over n is removed.

Using the triplet spin configuration in Eq. (12) and the property of s_{ez} and s_{hz} operators as $s_{ez} a_e(\pm \frac{1}{2}) = \pm \frac{1}{2} \hbar a_e(\pm \frac{1}{2})$ and $s_{hz} d_g(\pm \frac{1}{2}) = \mp \frac{1}{2} \hbar d_g(\pm \frac{1}{2})$, here again we find that only the contribution of Eq. (12b) is non-zero and then the operator in Eq. (41) becomes:

$$\hat{H}_{so}^{at(t)} \approx -\frac{2\hbar e^3 g Z \kappa}{\mu_x^2 c^2 \varepsilon r^2} \left(\frac{2\pi\hbar}{\varepsilon_0 \varepsilon V} \right)^{1/2} \sum_{\lambda} \frac{\sin \lambda}{\sqrt{\omega_{\lambda}}} e^{-i\omega_{\lambda} t} \times \left[\frac{1}{\sqrt{2}} (a_e (+1/2) d_g (-1/2) + a_e (-1/2) d_g (+1/2)) \right] c_{\lambda}^{\dagger} \quad (43)$$

It is to be noted here also that the operator ($s_{ez} + s_{hz}$) in Eq. (41) has flipped the spin of triplet sconfiguration (compare with Eq. (12b)) to a singlet configuration and hence the recombination can occur. Thus the mechanism of the occurrence of radiative recombination of triplet excitons through the new transition operator can be described in the following two steps:

1. The new operator is attractive for excitons so it attracts a triplet exciton to the heaviest atom as it is proportional to the atomic number. As the magnitude of attraction is inversely proportional to the square of the average distance between an electron and nucleus, only the nearest heavy nucleus will play the dominant role.
2. As soon as a triplet exciton interacts with such a spin-orbit-exciton-photon interaction, the spin gets flipped to a singlet configuration and exciton recombines radiatively by emitting a photon.

3.3. Rate of spontaneous emission from triplet excitons

We now consider a transition from an initial state $|i\rangle$ with a triplet exciton whose spin has been flipped by the spin-orbit interaction but it has no photons to a final state $|f\rangle$ with no excitation (ground state) and one photon created in a mode λ . These states in the second quantization are analogous to Eqs. (30) and (31), respectively. Using Eqs. (30) - (31) and the interaction operator in Eq. (43), the transition matrix element is obtained as:

$$\langle f | \hat{H}_{so}^{(t)} | i \rangle = -\frac{2\hbar e^3 g Z \kappa}{\mu_x^2 c^2 \varepsilon |r|^2} \left(\frac{2\pi\hbar}{\varepsilon_0 \varepsilon V} \right)^{1/2} e^{-i\omega_{\lambda} t} \frac{\sin \phi_{\lambda}}{\sqrt{\omega_{\lambda}}}, \quad (44)$$

Using Fermi's golden rule and the transition matrix element in Eq. (44), the rate of spontaneous emission of a photon from the radiative recombination of a triplet exciton in an organic solid/polymer denoted by R_{sp} (s^{-1}), can be written as:

$$R_{sp} = \frac{2\pi}{\hbar} \sum_{\lambda} |\langle f | \hat{H}_{so}^{(t)} | i \rangle|^2 \delta(E_{LUMO} - E_{HOMO} - \hbar\omega_{\lambda}), \quad (45)$$

where the sum over λ represents summing over all photon modes and E_{LUMO} and E_{HOMO} are the energies of the LUMO and HOMO energy levels. This can be evaluated in a way analogous to Eq. (33) and then we obtain:

$$R_{sp} = \frac{8e^6 g^2 Z^2 \kappa^2 \hbar \omega_{12}}{\mu_x^4 c^7 \varepsilon_0 \varepsilon^3 |r|^4}, \quad (46)$$

For triplet excitons using $|r| = a_x^T / \varepsilon$ and $g = 2$, the rate in Eq. (46) becomes [20]:

$$R_{sp} = \frac{32e^6 Z^2 \kappa^2 \varepsilon \hbar \omega_{12}}{\mu_x^4 c^7 \varepsilon_0 a_{ex}^4} \quad \text{s}^{-1} \quad (47)$$

For different phosphorescent materials only the atomic number of the heavy metal atom and the emitted energy will be different so the rate of spontaneous emission in Eq. (37) can be simplified as follows: Using $\varepsilon \approx 3$ which gives the triplet exciton Bohr radius $a_{ex} = 6a_0$ ($\mu = m_e$ and $\mu_x = m_e / 2$; m_e being the free electron mass), the rate in Eq. (47) can be expressed as:

$$R_{sp} \approx 25.3Z^2 (\hbar \omega_{12}) \quad \text{s}^{-1} \quad (\hbar \omega_{12} \text{ in eV}) \quad (48)$$

For phosphorescent materials like fac-tris (2-phenylpyridine) iridium (Ir(ppy)₃) and iridium(III) bis(2-phenyl quinolyl-N,C20) acetylacetonate (PDIr), where Ir has the largest atomic number $Z = 77$, other atomic numbers can be neglected being mainly of carbon. The rate in Eq. (48) depends linearly on the emission energy $\hbar \omega_{12}$ and other quantities are the same for all iridium doped materials. Thus, for iridium complexes doped in organic polymers the rate is obtained as: $R = 1.5 \times 10^5 \hbar \omega_{12} \text{ s}^{-1}$ ($\hbar \omega_{12}$ in eV). For green phosphor Ir(ppy)₃ has been doped for emission energy of 2.4 eV, for orange phosphor Ir(MMQ) [25] and FIrpic [4] have been doped for emission at 2.00 eV. In all these films the rate of spontaneous would be of the same order of magnitude ($3 - 4 \times 10^5 \text{ s}^{-1}$). This agrees quite well with the measured rate for Ir complexes [26].

Both rates of spontaneous emission derived in Eq. (37) on the basis of single electron excitation (atomic case) and that obtained in Eq. (46) for an electron-hole pair excitation have been applied to calculate it in organic solids and polymers [9, 27]. Apparently for platinum complexes Eq. (37) gives rates that agree better with experimental results but for iridium complexes Eq. (46) produces more favourable results.

In addition to developing the introduction of the phosphorescent materials to enhance the radiative recombination of triplet excitons, a step progression of HOMO and LUMO of the organic materials to confine the injected carriers within the emission layer has been applied [25]. This enables the injected e and h confined in a thinner space that enhances their recombination. This scheme has apparently proven to be most efficient so far.

Another approach for meeting the requirement of availing different energy levels for singlet and triplet emissions within the same layer of a WOLED is to incorporate nanostructures, particularly quantum dots (QDs), in the host polymers [28]. As the size of QDs controls their energy band gap, the emission energy can be manipulated by the QD sizes. It is found that the energy band gap of a QD depends on its size as [29]:

$$E_g(\text{eV}) = E_{g_{\text{bulk}}} + C / d^2 \quad (49)$$

where C is a confinement parameter and d is the size of a QD. Such a hybrid structures of organic host and inorganic QDs have been tried successfully [29-30]. It would be interesting if in future organic QDs could be grown on polymers and then the fabrication would be very cost effective.

This chapter is expected to present up to date review of the state-of-the art development in the theory of capturing emissions from triplet excitons in WOLEDs.

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