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Light emission from dark excitons in light emitting devices

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Applying the first order perturbation theory and a new time-dependent spin–orbit–photon interaction operator the rate of spontaneous emission from triplet (dark) excitons calculated in organic molecular solids, conjugated polymers and quantum dots is reviewed. The rates are found to be in good agreement with the experimental results in materials where the concept of Wannier–Mott type excitons is applicable, for example, in inorganic amorphous solids, conjugated polymers and quantum dots. In organic molecular solids or molecules, where Frenkel type excitons are formed, the calculated rates do not compare well with experiments. Application of the current theory is critically examined and discussed in light of the traditional approach of the second-order perturbation theory used for the triplet radiative recombination.

1 Introduction Radiative recombination of triplet excitons has attracted immense research interests due to its applications in electroluminescence [1], in particular in organic light emitting devices (OLEDs) [2–4]. This is because in inorganic crystalline semiconductors the exchange interaction between the excited electron and hole in an exciton is negligibly small due to being of narrow range [5]. It is the exchange interaction that separates the singlet and triplet exciton energy states. In these materials excitons have large orbital radius, known as large orbital radii excitons with vanishingly small exchange interaction. Therefore in these semiconductors singlet and triplet excitons are difficult to observe separately. However, triplet exciton emission has been observed in inorganic amorphous semiconductors [6], quantum dots [7, 8] and several conjugated polymers used in OLEDs [2–4]. In these semiconductors the energy difference, ΔE_{ST}, between the singlet and triplet excitons varies from a few meV to fraction of an eV. For example, in many conjugate polymers, ΔE_{ST} is found to be nearly constant at about 0.7 eV [2, 3, 9, 10]. It has been established that Wannier–Mott type excitons are formed in inorganic amorphous semiconductors [11]. The concept may also be extended to conjugated polymers because of the long chain structure.

The problem with a triplet excitation is that its radiative recombination (phosphorescence) through dipolar transitions is spin forbidden, in contrast to singlet excitations where radiative recombination (photoluminescence) is spin allowed. A triplet radiative transition is known to occur through the spin–orbit interaction that flips the spin to facilitate the recombination. As the spin–orbit interaction is proportional to the atomic number it is weak in hydrocarbons and polymers, resulting in inefficient emission from a triplet exciton in such materials. Therefore, in light emitting devices (LEDs), one would like to have emissions only from singlet excitons. However, statistically singlet and triplet excitons are generated in the ratio of 1 : 3 [2] in LEDs, which limits their efficiency to 25% at most. It is therefore very important to make the triplet emission as efficient as possible and for doing this one needs to understand quantitatively the mechanism of a triplet exciton radiative recombination in any material first.

The well known spin–orbit interaction operator is a stationary operator [12], not a time-dependent transition operator and hence it cannot cause any optical transition. In aromatic molecules and molecular crystals, like naphthalene, anthracene, etc., the radiative emission from triplet excitations has been studied [13–17] a few decades ago. In some work, the time-dependent interaction operator used then consisted of higher order interactions, such as spin–spin interaction, whose contributions were negligibly small and hence the calculated radiative lifetime from the first order perturbation theory was found to be much longer than that measured experimentally [14].

In the absence of a proper time-dependent spin–orbit–photon transition operator, a very long standing tradition has been set up to calculate the transition matrix element between an excited triplet and singlet ground state in two steps [14, 17–19]. In the first step, applying the first order perturbation theory, the stationary spin–orbit interaction operator is used to calculate the energy splitting in a degenerate triplet state and the first order perturbed wave function of the triplet state is expanded as a linear combination of all singlet and triplet unperturbed wave functions. In the second step, then the time-dependent dipole transition operator is used to calculate the transition matrix element between the expanded first order triplet state and singlet ground state wave functions. In this way one gets fractional non-zero matrix element contributed by the singlet components in the expansion of triplet wave function. This approach has been applied to aromatic molecules by many and varying results have been obtained [14–20]. Li and Lim [21] have measured radiative lifetime in many aromatic molecules and Adrian [18] has calculated it semiemperically applying the traditional approach and among all, to the best of our knowledge, this work has produced results closest to the experiments. Some recent works, however, have applied the traditional approach on conjugated polymers [19] and non-planar aromatic heterocyclic molecules [20]. As the two-step process is equivalent to a second order perturbation theory, one wonders why there exists no spin–orbit–photon interaction operator for the triplet emission like the dipole transition operator for singlet emission.

However, as it has recently been pointed out [12] that the traditional approach cannot be applied to triplet Wannier–Mott type excitons where both singlet and triplet states arise from the first excited (s-state with angular momentum quantum number being zero) state of an exciton bound in hydrogenic states and only the spin configurations are different for singlet and triplet excitons. A new time-dependent spin–orbit–photon interaction operator [12] has recently been derived by one of the authors and is used to calculate the transition matrix element between a triplet excitation state and the singlet ground state through the first order perturbation theory in many amorphous solids [22] and conjugated polymers [23]. The approach has also been extended to molecular crystals, like naphthalene and anthracene. Although the radiative lifetime calculated from the new operator agrees very well for amorphous semiconductors and conjugated polymers, it does not agree so well with experiments for molecular solids because the concept of the Wannier–Mott excitons is not applicable in molecular crystals [5].

In this paper, the newly developed recent theory is extended to calculate the rate of spontaneous emission in quantum dots and found to be in reasonable agreement with experiments. In addition, the cause of the discrepancy between the theoretical results and experimental ones are critically analysed and discussed.

2 Rate of spontaneous emission from triplet excitons For triplet excitons two expressions are derived for the rate of spontaneous emission within the two level approximation [9–12]. The first one that can be applied to a triplet excitation in any atoms or molecules is given by [12, 23]:

$$R_{\mathrm{sp}} = \frac{e^6 Z^2 \kappa^2 \hbar\omega_{12}}{2\mu_x^4 c^7 \varepsilon_0 |r|^4}\ , \quad \kappa = (4\pi\varepsilon_0)^{-1}\ , \tag{1}$$

where Z is the atomic number of the atom or constituting atoms in a homonuclear molecule. For molecules consisting of hetero-atoms the atomic number of the heaviest atom should be used. In some cases, where heteroatoms are not very different in their atomic numbers, the average atomic number will be more appropriate to use [12]. $\hbar\omega_{12} = E_2 - E_1$ is the energy of the emitted photon. E_2 is the energy of the triplet state of excitation and E_1 is the energy of the ground state. $|r|^{-2} = \sum_{n=1}^{N} C_n^{\mathrm{H}*} C_n^{\mathrm{L}} \langle \varphi_{\mathrm{H}n} | r_{\mathrm{e}n}^{-2} | \varphi_{\mathrm{L}n} \rangle$, where $|r|$ is the average separation between excited electron and hole before their radiative recombination, $\varphi_{\mathrm{H}n}$ and $\varphi_{\mathrm{L}n}$ are the atomic orbitals of the n-th atom and C_n^{H} and C_n^{L} are the corresponding probability amplitude coefficients of HOMO and LUMO (triplet), respectively.

The second expression that can be applied to triplet Wannier–Mott type excitons bound in hydrogenic states in solids, is given by:

$$R_{\mathrm{sp}} = \frac{e^6 Z^2 \kappa^2 \hbar\omega_{12}}{2\mu^4 c^7 \varepsilon_0 \varepsilon^3 a_0^4}\ , \tag{2}$$

where $|r|$ in Eq. (1) is replaced by $|r| = a_x/\varepsilon$, with a_x is the excitonic Bohr radius of a triplet exciton given by $a_x = \mu\varepsilon/\mu_x a_0$ [4], $a_0 = 0.0529$ nm is the Bohr radius, ε is the static dielectric constant of the solid and μ is the reduced mass of electron ($\mu = m_{\mathrm{e}}$) in the hydrogen atom. The rate in Eq. (2) depends only on three material properties, the atomic number Z, emitted photon energy $\hbar\omega_{12}$ and the dielectric constant ε.

Equation (2) can be used to calculate the triplet emission rates only in bulk materials but not in quantum dots (QDs) because it does not take into account the effect of confinement. It is established that the exciton binding energy in QDs gets enhanced due to the confinement, especially in QDs of size smaller than the excitonic Bohr radius in bulk. As the exciton binding energy is inversely proportional to the excitonic Bohr radius (separation between e and h in an exciton), one may define an effective exciton Bohr radius in QDs, which may be regarded to shrink from its value in bulk in proportion to the enhancement in the exciton binding energy. If the enhancement factor α is defined as the ratio of the exciton binding energy in a QD to that in bulk, the effective excitonic Bohr radius a_x^{D} in a QD can be given by $a_x^{\mathrm{D}} = a_x/\alpha$. Using this in Eq. (2), the rate of triplet exciton emission for QDs $R_{\mathrm{sp}}^{\mathrm{D}}$ is obtained as:

$$R_{\mathrm{sp}}^{\mathrm{D}} = \alpha^4 R_{\mathrm{sp}} \,, \tag{3}$$

where R_{sp} is the rate in bulk [Eq. (2)]. Thus the confinement plays a very significant role in the triplet recombination in QDs.

3 Results The rate derived in Eq. (3) is applied to calculate the radiative lifetime of triplet excitons in single CdSe/ZnS quantum dots [7] and self-assembled InAs quantum dots [8]. The triplet exciton emission energy observed in single CdSe/ZnS quantum dots (QDs) of radius 1.5 nm is 2.31 eV and of radius 5.6 nm is 1.94 eV. The effective masses of electrons and holes are found to be $0.235m_{\mathrm{e}}$ and $1.35m_{\mathrm{e}}$ [24], respectively, which give the excitonic reduced mass $\mu_x = 0.2m_{\mathrm{e}}$ and excitonic Bohr radius $a_x = 2.35$ nm with $\varepsilon = 8.9$ [25]. For using Eq. (3), we also need the confinement factor α. The enhancement in the binding energy in CdS QDs has been studied [26], accordingly the exciton binding energy in a QD of radius 1 nm gets enhanced by a factor $\alpha = 10/3$ at a barrier height of 500 meV, 5 meV at 1000 meV and 7 meV at 2250 meV. The bulk exciton binding energy in CdS is 60 meV [26]. There are no such data known for CdSe QDs to the auhtor's knowledge as a result these are used here to estimate the triplet radiative rates in CdSe QDs as well. Using these and $Z = 48$ (Cd) in an Eq. (3) we get $R_{\mathrm{sp}}^{\mathrm{D}} = 1.2 \times 10^4\ \mathrm{s}^{-1}$ and radiative lifetime, $\tau_{\mathrm{r}} = 1/R_{\mathrm{sp}} = 83$ µs at $\alpha = 10/3$, $R_{\mathrm{sp}}^{\mathrm{D}} = 6.1 \times 10^4\ \mathrm{s}^{-1}$ and radiative lifetime, $\tau_{\mathrm{r}} = 1/R_{\mathrm{sp}} = 16.4$ µs at $\alpha = 5$ and $R_{\mathrm{sp}}^{\mathrm{D}} = 2.3 \times 10^5\ \mathrm{s}^{-1}$ and radiative lifetime, $\tau_{\mathrm{r}} = 1/R_{\mathrm{sp}} = 4.2$ µs at $\alpha = 7$, which qualitatively agree with the observed lifetime of 1 µs [7]. If one changes the photon energy to 1.94 eV for QDs of radius 5.6 nm one would still get the radiative lifetime of the same order of magnitude because similar confinement factors [26] will be applicable. However, it is not possible to make any quantitative comparison without knowing the confinement factor more precisely.

In InAs self assembled QDs, the emitted triplet energy is 1.2 eV [8] for QDs of radius 1.00 nm. Using the electron and hole effective masses as $0.02m_{\mathrm{e}}$ and $0.4m_{\mathrm{e}}$ [24], respectively, we get $\mu_x = 0.019m_{\mathrm{e}}$ and $a_x = 40.37$ nm with $\varepsilon = 14.5$. For InAs, $Z(\mathrm{In}) = 49$ is not very different from Cd (48) in CdSe but the dielectric constant of InAs is relatively large. Therefore if the same confinement factors are used as for CdSe, according to Eq. (2) the rates are expected to be smaller and the corresponding radiative lifetimes longer than in CdSe QDs. The experimental value is 10 ns, which includes the non-radiative component as well and usually the non-radiative components are much faster. Nonetheless, it is difficult to compare quantitatively without knowing the radiative lifetime exclusively and precisely.

Table 1 Radiative lifetime calculated from the inverse of the rate of spontaneous emission given in Eq. (3) for CdSe/ZnS. Only the radiative lifetime with $Z = 48$ and the confinement factor $\alpha = 7$ is given here, others are discussed in the text. The radiative lifetime of inorganic semiconductors and conjugated polymers are listed from the corresponding references using the material parameters published there.

materials	τ_{r} (s)	exptl. (s)
CdSe/ZnS QD	4.2×10^{-6}	10^{-6} [7]
a-Si : H	5×10^{-3} [12]	10^{-3} [6]
a-$\mathrm{As_2Se_3}$	0.7×10^{-4} [22]	10^{-4} [6]
a-$\mathrm{As_2S_3}$	2.8×10^{-4} [22]	10^{-4} [6]
P1 (polymer)	1.82×10^{-4} [23]	1.7×10^{-4} [10]
P2 (polymer)	1.96×10^{-4} [23]	5.0×10^{-4} [10]
P3 (polymer)	2.17×10^{-4} [23]	5×10^{-4} [10]
naphthalene	2.2 [23]	36.2 [21]

The calculated values of the radiative lifetime in CdSe/ZnS QDs are listed in Table 1 at $\alpha = 7$ along with the results of a few amorphous semiconductors and conjugate polymers incorporated with platinum atoms. Experimental values are also listed. In addition, the radiative lifetime for naphthalene molecular crystal is also listed. It may be noted that while the agreement of theoretical results with experiments is quite good in amorphous inorganic semiconductors, conjugated polymers and quantum dots, the theoretical radiative lifetime in naphthalene does not agree that well with the experimental value. This discrepancy will be discussed further in the next section.

4 Discussions The rate of spontaneous emission from triplet excitons and the corresponding radiative lifetimes are estimated for two CdSe/ZnS and InAs QDs using the new spin–orbit–photon interaction operator and first order perturbation theory. Table 1 shows that the calculated radiative lifetime in CdSe/ZnS QD with $Z = 48$ (Cd) and confinement $\alpha = 7$ agrees reasonably well with the experimental result. However, for a hetero atomic solid, with not very different atomic numbers, one should use the average value of Z. For CdSe, the average $Z = (48(\mathrm{Cd}) + 34(\mathrm{Se}))/2 = 41$, using this the rates of spontaneous emission and the corresponding radiative lifetimes are obtained as $R_{\mathrm{sp}}^{\mathrm{D}} = 8.6 \times 10^3\ \mathrm{s}^{-1}$ and radiative lifetime, $\tau_{\mathrm{r}} = 1/R_{\mathrm{sp}} = 116$ µs at $\alpha = 10/3$, $R_{\mathrm{sp}}^{\mathrm{D}} = 4.4 \times 10^4\ \mathrm{s}^{-1}$ and $\tau_{\mathrm{r}} = 1/R_{\mathrm{sp}} = 22.9$ µs at $\alpha = 5$ and $R_{\mathrm{sp}}^{\mathrm{D}} = 1.7 \times 10^5\ \mathrm{s}^{-1}$ and $\tau_{\mathrm{r}} = 1/R_{\mathrm{sp}} = 5.9$ µs at $\alpha = 7$. These radiative lifetimes are slightly larger than those obtained in Table 1 with $Z = 48$. For InAs the average Z is the same as for CdSe and hence it will give similar results.

As it can be seen from Table 1, the calculated radiative lifetime agrees quite well with experimental results in CdSe/ZnS QDs, conjugated polymers and inorganic amorphous semiconductors. However, it does not agree so well in organic molecules, e.g., naphthalene. A similar discrepancy is also obtained for anthracene not listed here. As the original theory of deriving the new operator is applicable for an excited electron hole pair bound in Wannier–Mott type excitonic states, the rate obtained from Eq. (2) may not be applicable for organic molecules and also for organic solids where Frenkel or molecular excitons concept is more suitable. For organic molecules, as stated above, one should use the rate in Eq. (1) and in that use $|r|$ calculated from the HOMO and LUMO molecular orbitals.

We have calculated HOMO and LUMO molecular orbitals of naphthalene using the standard software and then using the single atomic orbitals (AOs) evaluated $|r|^{-2}$ as outlined above. For naphthalene, the energy difference between HOMO and LUMO is found to be $\hbar\omega_{12} = 7.56$ eV and $|r|^{-2} = 4.32 \times 10^{14}$ m^{-2}, which gives $R_{sp} = 4.1 \times 10^{-9}$ s^{-1} and $\tau_r = 2.4 \times 10^8$ s in comparison with the experimental value of 36 s (Table 1) measured experimentally and 69 s calculated through the traditional approach theoretically [18]. From this point of view, $\tau_r = 2.2$ s obtained from Eq. (2) (Table 1) agrees better with the experiment. This discrepancy is a clear indication of the fact that the simplified rate of Eq. (1) cannot be applied for organic molecules without taking into account the influence of the molecular structure. The importance of the molecular structure is evident from the work of Adrian and also more recent work of Schmidt et al. [20] on nonplanar aromatic heterocyclic molecules.

However, for amorphous solids and conjugated polymers, the new rate in Eq. (2) and for QDs the rate in Eq. (3) are easy to apply and produce satisfactory results in comparison with experiments.

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