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Missing links for triplet radiative recombination in light emitting devices[♣]

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Light emission from triplet excitons in light emitting devices (LED) is reviewed. The rate of spontaneous emission of triplet excitons is presented in inorganic amorphous semiconductors, molecular crystals and conjugated polymers containing platinum atoms in the chain. It is shown that the recently discovered new time-dependent spin-orbit-photon interaction operator is responsible for the radiative emission from triplet excitations in materials, and the transition occurs due to flipping of the spin. The rate depends on the square of the atomic number of the constituting atoms. The calculated rates and corresponding radiative lifetime agree very well with the known experimental results in conjugated polymers and inorganic amorphous semiconductors. Rates in molecular crystals are compared with those obtained from the traditional theory.

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1. Introduction

Photoluminescence studies in both inorganic and organic amorphous semiconductors have continued to attract research interest because of their commercial applications in light emitting devices (LEDs). In particular, the discovery of electroluminescence from conjugated polymers [1] has generated immense research interest in the field of organic light emitting devices (OLEDS)[2-4]. Although the phosphorescence from triplet excitons is not significant in bulk crystals of inorganic semiconductors, because of the short range exchange interaction between the excited electrons and holes, both singlet and triplet radiative emissions have been observed in bulk amorphous semiconductors [5-6] and organic conjugated polymers [4]. Photoluminescence (PL) from singlet excitons with anti-parallel spins of electron and hole (e-h) is spin allowed through dipole transitions and the rate of dipolar transition can be calculated from the first order time-dependent perturbation theory [7]. However, in a triplet exciton, the electron and hole (e-h) have parallel spins and hence their radiative recombination (phosphorescence) through dipolar transitions is spin forbidden. A triplet radiative transition can only occur through the mediation of the spin-orbit interaction that can flip the spin to facilitate the recombination. This results in inefficient radiative emission from triplet excitons. From this point of view, in light emitting devices, one would like to have emissions only from singlet excitons. However, the operation of LEDs brings electrons and holes together from opposite electrodes, and statistically should generate singlet and triplet excitons in the ratio 1:3 [3]. Accordingly, where triplet emission is not possible, LEDs are limited to only 25% efficiency at the most. It is therefore very important to understand the mechanism of the radiative recombination of triplet excitons in any material used for fabricating LEDs and OLEDs.

The exciton-photon interaction operator that is used as a perturbation for the radiative recombination of singlet excitons is given by [7]:

$$\hat{H}_{xp} = -\frac{e}{\mu_x}\mathbf{A}.\mathbf{p} \,, \tag{1}$$

where e is the electronic charge, $\mathbf{A}$ is the vector potential of radiation, $\mathbf{p} = -i\hbar\nabla_r$ is the linear momentum associated with the relative motion between the electron and hole in an exciton and μ_x is the excitonic reduced mass. $\hat{H}_{xp}$ is spin independent and hence the transition matrix element between a singlet excited state to singlet ground state is non-zero. However, it is zero between the triplet excited state and singlet ground state. Therefore, the operator in Eq. (1) cannot be used for calculating the rate of radiative emission from triplet excitons. Until recently [8], there was no other exciton-photon interaction operator known in the literature to calculate the rate of radiative emission from triplet excitons. In the absence of such a time-dependent transition operator, a long established tradition has been set up to use first the stationary spin-orbit interaction operator and first order perturbation theory to

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[♣] Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 split the degeneracy of a triplet state and expand the perturbed triplet state wave functions in terms of all triplet and singlet state wave functions. Then in the second step, the exciton-photon interaction operator in Eq. (1) is used to calculate the transition matrix element between the first-order perturbed wave function of the triplet excited state thus obtained above and the singlet ground state wave function. In this way the transition matrix elements between the singlet state wave function terms in the perturbed wave function and the singlet ground state wave function are found to be non-zero and can be calculated. Using these non-zero contributions to the transition matrix element and Fermi's golden rule, the rate of spontaneous emission is then calculated [9, 10]. This traditional approach is equivalent to the second-order perturbation theory.

However, there are the following problems with this approach in its application to excitons: 1) The well known stationary spin-orbit interaction of an electron in an atom is given by $\hat{H}_{so} = \frac{Ze^2}{2m_e^2 c^2 r^3}\mathbf{s}.\mathbf{L}$, where Z is the atomic number, e and m_e are electronic charge and mass, respectively, c is the speed of light and r is the distance of an electron from the nucleus. **s** and **L** are the spin and orbital angular momenta of the electron, respectively. $\hat{H}_{so}$ is zero for $\mathbf{s} = \mathbf{L} = \mathbf{0}$, i.e., for all *s*-state orbitals with $l = 0$ and also for singlet excitations. As such, it cannot contribute to the radiative recombination of Wannier-Mott type of triplet excitons where both singlet and triplet exciton states arise from the first excited *s*-state (n =1 and l =0). Therefore, the traditional approach cannot be applied to triplet Wannier-Mott type excitons where the emission occurs from the first excited state. One may argue that in condensed matter, the excited electrons and holes move around the nuclei so they have non-zero L in a triplet state which needs to be taken into account. However, this non-zero L giving rise to the stationary spin-orbit interaction cannot cause any transition. 2) The spin-orbit interaction is expected to flip the spin from a triplet configuration to the singlet configuration to facilitate the transition, but it is not apparent how that can occur through the traditional approach because the actual transition occurs through the dipole interaction operator which is independent of spin, not the spin-orbit interaction operator. 3) As for singlet excitons Eq. (1), why is no triplet exciton-photon interaction used to calculate the transition matrix element directly from the first-order perturbation theory? 4) It has been observed that the incorporation of heavy metals like palladium and platinum into the chain of several π-bonded polymers and the doping of host materials with triplet acceptors containing heavy metal atoms increases the efficiency of phosphorescence [2-4, 11-14] in these materials, proportional to the atomic number of the heavy metal atom (Z^2). This enhancement cannot be explained directly from the traditional approach, because except for the stationary spin-orbit interaction which on its own cannot cause any transition, no other transition operator depends on the atomic number.

The present author [8] has recently derived a new time-dependent spin-orbit-photon interaction and used it to calculate the rate of spontaneous emission from triplet excitons in non-crystalline inorganic semiconductors. The calculated radiative lifetime of triplet excitons in hydrogenated amorphous silicon is found to agree well with the experimental results. The theory has also been extended to calculate the rates of spontaneous emission and corresponding radiative lifetimes in amorphous chalcogenide glasses [15] and calculated results are found to be in good agreement with experimental ones. The derived rate of spontaneous emission from the new triplet-spin-orbit interaction operator has also been recently used to calculate the radiative rate of emission from triplet excitations in conjugated polymers incorporating platinum atoms in their structure [10,16] and rates are found to agree quite well with the observed ones.

In this paper, the application of the new theory [8] of radiative decay of triplet excitons is reviewed, and results are analyzed in different materials. Two types of rates of spontaneous emission of triplet excitons are derived: 1) can be applied to atoms and molecules and 2) applies to solids where the Wannier-Mott type excitonic picture can be applied. Results obtained for different materials are compared with experiments as well as those obtained from the traditional theory, wherever applicable.

2. Triplet exciton-spin-orbit-photon interaction operator

The recently derived time-dependent spin-photon interaction operator [8] for a molecular excitation in a molecule can be written as:

$$\hat{H}_{so} = -\frac{eg}{2\mu_x^2 c^2}\left(-\frac{e}{c}\sum_n \mathbf{s}\cdot(\mathbf{A}\times\nabla V_n)\right), \qquad (1)$$

where $g = 2$, is the gyro magnetic ratio and μ_x is the excitonic reduced mass ($\mu_x^{-1} = m_e^{*-1} + m_h^{*-1}$). **A** is the vector potential of photons acting on electron, V_n is the scalar potential of the n^{th} nucleus acting on the excited electron. Within the so called dipole approximation ($e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} \approx 1$), the vector potential is given by $\mathbf{A} = \sum_\lambda A_0 \hat{\varepsilon}_\lambda c_\lambda^+ e^{-i\omega_\lambda t} + c.c.$, where $A_0 = \left[\frac{2\pi c^2 \hbar}{\varepsilon_0 \varepsilon \omega_\lambda V}\right]^{1/2}$, $\hat{\varepsilon}_\lambda$ is the unit polarization vector, c_λ^+ is the creation operator of a photon in mode λ, ε_0 is the vacuum permittivity, ε is the static dielectric constant of the material, ω_λ is the photon's frequency and V is the illuminated volume. Here *c.c.* represents the complex conjugate of the first term and it corresponds to the absorption of a photon, which will not be considered here.

The scalar nuclear potential V_n is given by $V_n = \frac{Z_n e\kappa}{\varepsilon r_n}$, $\kappa = 1/4\pi\varepsilon_0$ and $\nabla V_n = -\frac{Z_n e\kappa}{\varepsilon r_n^3}\mathbf{r}_n$, where Z is the atomic number of the atom, $\mathbf{r}_n$ is the position vector of the electron from the n^th^ nucleus, $|\mathbf{r}_n| = r_n$. For $Z_n > 1$, the interaction between the excited electron and other valence electrons in an atom is considered to be negligible [8].

As terms within the summation sign depend on the inverse square of the distance of the electron from a nucleus, the nearest nucleus is expected to have the dominant influence, and the presence of other nuclei may then be neglected. Within this approximation, Z_n may be replaced by Z, an average site independent atomic number. However, this approximation is valid only for solids with atoms of not very different atomic numbers. In the case of hydrocarbons, only the atomic number of carbon is necessary to use. If a molecule contains heavier atoms, the atomic number of the heaviest atom should be used in the calculation.

3. Rate of spontaneous emission from triplet excitations

3.1 In molecules

Using equation (1), the rate of spontaneous emission within the two level approximation for a triplet excitation in a molecule is obtained as [8]:

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

where $\hbar\omega_{12} = E_2 - E_1$ is the energy of the emitted photon, where E_2 is the energy of the triplet state of excitation and E_1 is the energy of the ground state or valence band. $|r|^{-2} = \sum_{n=1}^{N} C_n^{H*} C_n^{L} < \varphi_{Hn} | r_{en}^{-2} | \varphi_{Ln} >$, where $|r|$ is the average separation between the excited electron and hole before their radiative recombination, φ_{Hn} and φ_{Ln} are the atomic orbitals of the n^th^ atom and C_n^H and C_n^L are the corresponding probability amplitude coefficients of the HOMO and the lowest excited triplet exciton state, respectively.

3.2 In molecular solids and conjugated polymers

In organic molecular solids and conjugated polymers, where the triplet excitation state lies much below the conduction band edge, the two-level approximation can be applied and the rate obtained in Eq. (1) can be used. However, the calculation of the average separation, $|r|$, as outlined above can be quite complicated, particularly for conjugated polymers with long chains. In that case, a better approach is to use $|r| = a_x / \varepsilon$, where a_x is the excitonic Bohr radius of a triplet exciton given by $a_x = \frac{\mu\varepsilon}{\mu_x} a_0$ [8,15], $a_0 = 0.0529$ nm is the Bohr radius and μ is the reduced mass of electron in the hydrogen atom. Substituting this in equation (2), the rate of spontaneous emission from a triplet excitation in molecular semiconductors and polymers is obtained as:

$$R_{sp} = \frac{e^6 Z^2 \kappa^2 \varepsilon \hbar\omega_{12}}{2\mu_x^4 c^7 \varepsilon_0 a_x^4}. \tag{3}$$

It should be remembered here that the expression for the excitonic Bohr radius a_x defined above is valid only for Wannier-Mott type excitons and replacing a_x by its expression makes the rate of spontaneous emission in Eq. (3) independent of the excitonic reduced mass, μ_x, and then the rate depends on only three material dependent parameters, Z, $\hbar\omega_{12}$ and the dielectric constant ε. 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. Their radiative lifetime is calculated from the inverse of the rate in equation (3), $\tau_R = 1/R_{sp}$.

3.3 In amorphous semiconductors

In amorphous semiconductors, the two-level approximation cannot be applied due to the presence of the localized tail states within the band gap [17]. In this case, four possibilities of transitions exist [8,15]: i) both the excited electron (e) and hole (h) are in their respective extended states (conduction and valence bands), ii) e is in the extended (conduction) and h in the tail states, iii) e is in the tail and h in extended states (valence band) and iv) both e and h are in their respective tail states. The rates derived for the possibilities (i) to (iii) are obtained as [8,15]:

$$R_{sp}^{a-sem} = \frac{16 e^6 g^2 Z^2 k^2 \varepsilon}{\varepsilon_0 \mu_x c^4 a_x^4 (\hbar\omega_\lambda) \hbar^3 \nu \rho_A} (\hbar\omega_\lambda - E_0)^2 \times \exp[-(\hbar\omega_\lambda - E_0)/\kappa_B T] \Theta(\hbar\omega - E_0) \tag{4}$$

where $\hbar\omega_\lambda$ is the emitted energy of a photon in mode λ, ν is the number of coordinating valence electrons per atom and ρ_A is the atomic density per unit volume. A step function $\Theta(\hbar\omega_\lambda - E_0)$ is used to indicate that there is no radiative recombination for $\hbar\omega_\lambda < E_0$; $E_0 = \frac{(1+\beta)E_{mx} - 2}{(1+\beta)}$, where $\beta = 1/\kappa_B T$ and E_{mx} is the energy at which the peak of the triplet photoluminescence is observed and T is the temperature.

For the possibility (iv), denoting the spontaneous emission rate in the tail-states by R_{spt}^{a-sem}, it is obtained as:

$$R_{spt}^{a-sem} = R_{sp}^{a-sem} \exp[-2t'_e a_{ex}]\,, \tag{5}$$

where

$$|\,\mathbf{t}'_e\,| = t'_e = \sqrt{2m_e^*(E_c - E_e)}\,/\,\hbar\,, \tag{6}$$

with m_e^* being the effective mass of an electron in the conduction tail states with energy E_e and E_c is the energy of the electron mobility edge. The exponential factor in Eq. (5) arises due to the localization of the electron and hole wave functions in the tail states and the pre-exponential factor is the same as the rate in Eq. (4).

4. Results

The rate of spontaneous emission derived in equation (3) is used to calculate the rates in naphthalene crystals and three conjugated polymers, P1, P2 and P3 chosen from [12] containing platinum in the polymer chain for which the rates of radiative recombination have been measured. For all polymers considered from ref. [12] and naphthalene crystals, 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 $a_x = \frac{m_e \varepsilon}{\mu_x} a_0 = 6a_0$. We can calculate the radiative rates for all the polymers studied in [12] 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 incorporating platinum atoms, the rates of radiative recombination in P_1, P_2 and P_3 are found to be of the order of 10^3 s^{-1}, which agrees very well with the experimental results [12].

For calculating the rates in a-Si:H, it is well established that the non-radiative relaxation of charge carriers is much faster, in the ps time range [17], than in crystalline Si. Therefore, it is expected that PL occurs after at least holes have relaxed to the tail states, which means we should look at the rates of spontaneous emission only from the possibilities (ii) to (iv). The effective masses of electrons in the conduction and holes in the valence band are found to be equal in sp^3 hybrid semiconductors like a-Si:H [8] as given in table 2. Other material dependent quantities used in the calculation are also listed in the caption of table 2. For a-Si: H, a-As$_2$Se$_3$, a-As$_2$S$_3$ and a-Se we have used Z = 14, 33.6, 33 and 34, respectively, in the calculation of rates from Eqs (4) and (5). The results obtained compare very well with the experimental results of Aoki et al. [18].

For amorphous chalcogenides (a-Chs) (a-As$_2$Se$_3$, a-As$_2$S$_3$ and a-Se), due to the interaction of lone pair orbitals, the effective masses for the possibilities (ii) and (iii) are found to be different [15], as given in table 2. For a-Chs also the rates are calculated and compared with the experimental results only for possibilities (ii) - (iv).

Table 1. Assuming $m_e^* = m_h^* = m_e$, *which gives* $\mu_x = 0.5m_e$ *and taking* $\varepsilon = 3$, *the rates of spontaneous emission are calculated from Eq. (3) for the molecular crystal of naphthalene (Nap) and three conjugated polymers (P1, P2, P3). Using these, the triplet excitonic Bohr radius becomes* $a_x = 6a_0$.. *The observed lifetime of triplet excitons in naphthalene is 2.5 s[22]* [a]Ref. [22], [b]Ref. [12], [c]Ref[13].

	$\hbar\omega_{12}$ (eV)	R_{sp} (s^{-1}) Eq. (3)	$R^{\exp}$ (s^{-1})^c	τ_R (s)
Nap	2.61^a	0.45	-	2.2
P1	2.40^b	5.5x10^3	6x10^3	1.82x10^{-4}
P2	2.25^b	5.1x10^3	1.8x10^3	1.96x10^{-4}
P3	2.05^b	4.6x10^3	1x10^3	2.17x10^{-4}

5. Discussion

Using a new time-dependent perturbation operator for the spin-orbit-photon interaction, the rates of radiative recombination of triplet excitations are derived from the first order perturbation theory for molecular solids, conjugated polymers and amorphous semiconductors. The derived rate is then used to calculate the rates of radiative emission from triplet excitations in naphthalene crystals, platinum conjugated polymers (P1, P2 and P3) incorporating platinum and amorphous semiconductors. The calculated rates agree very well with the observed rates in these materials (see tables 1 and 2). Without the inclusion of Pt (Z = 78) in the host conjugated polymers, the rate with mainly carbon atoms with Z = 6 is found to be about 46 s^{-1}, which is at least two orders of magnitude less. This enhancement in the recombination rate due to the doping of the organic LED matrix agrees very well with the observed enhancement in electroluminescent devices [8].

The radiative rate derived in equation (3) increases with the triplet state energy, which also agrees with the observed increase in several polymers [12]. Therefore, this work may be regarded to have resolved two long standing issues: 1) It provides a correct time-dependent spin-orbit-photon interaction operator for triplet excitons that was not known until recently, and 2) the rate of radiative recombination can be calculated from the first order perturbation theory.

In naphthalene crystals, however, although the calculated radiative lifetime of 2.0 s agrees well with the measured lifetime of 2.5 s, the measured lifetime is the total lifetime τ, which is largely influenced by the non-radiative recombination ($1/\tau = R_{sp} + R_{non-rad}$) [16]. In this case, the radiative lifetime has been measured by Li and Lim [19] as 61 s, which agrees quite well with the calculated value of 69 s through the traditional approach by Adrian [20]. Using the traditional approach, Henry and Siebrand [9] have also calculated the radiative triplet lifetime in naphthalene as 10 s, as has recently been pointed out [10]. Although these two results obtained from the traditional approach are quite different from each other, in comparison they agree more closely with the experimental result of the radiative lifetime in naphthalene than the calculated radiative lifetime of 2 s obtained from the present approach. This difference may be found to be true for most organic materials [19, 20] and one may be inclined to think that the results from the new operator do not work for molecular crystals. This contradiction needs to be explored very carefully before drawing any general conclusions. In materials like naphthalene, anthracene, etc., many spectroscopic measurements are carried out on molecules but their results are also used for their crystalline counterparts. This is no problem for molecular crystals where the intermolecular interactions in the crystalline form are weak, leading to narrow bandwidths, and therefore the electronic properties are not very different between molecules and crystals. As a result, excitons in these materials are termed as molecular excitons, Frenkel excitons, or small radii orbital excitons [21]. Why should this make any difference in the application of the new interaction operator to these materials? This is explained below:

The rates given in table 1 are calculated using the rate in Eq. (3), in which the average separation |*r*| between the excited e-h pair is replaced by the excitonic Bohr radius derived for Wannier-Mott excitons as:

$$a_x = \frac{m_e \varepsilon}{\mu_x} a_0 \quad . \tag{7}$$

As stated above, if one substitutes Eq. (7) in Eq. (3), the resulting rate thus obtained from Eq. (3) depends only on three material dependent quantities , Z , $\hbar\omega_{12}$ and the static dielectric constant ε. However, the concept of Wannier-Mott excitons is not valid for organic molecular crystals or molecules, as explained above. Therefore, for calculating the rates in aromatic molecules and molecular crystals one should use the expression for the rate in Eq. (2) by calculating |*r*| from the HOMO and LUMO wave functions. Unfortunately, this has not yet been done but such calculations deserve attention for future work. Needless to say, the rate is very sensitive to |*r*| and even a small change can make a big difference in it. For the reason given above for molecular solids, it may be desirable to address the applicability of the rate in Eq. (3) with a two level approximation for triplet excitons in conjugated polymers. Here, excited e and h can travel smoothly along the chain so the concept of Wannier-Mott excitons may be acceptable. For the validity of the two-level approximation, one may consider the following. The triplet exciton state located at an energy difference of 0.7 eV below the singlet exciton state is really far away from the conduction band. From this point of view, the two level approximation may be considered to be fully justified. The calculated rates of radiative recombination of triplet excitons for polymers have been obtained through two approaches: a) using $\mu_x = 0.5 m_e$ and $a_x = 6 a_0$, and b) using the calculated μ_x and the root mean square value of the separation between e and h [14, 16] and they agree reasonably well. This may be regarded as further support for the validity of the approximation of two level systems for polymers.

Table 2. Rates calculated using Eq. (4) for possibilities (ii) and (iii) and Eq. (5) for the possibility (iv) are listed for four amorphous semiconductors, a-Si:H, a-As_2Se_3, a-As_2S_3 and a-Se with $\rho_A = 5 \times 10^{28}$ m^{-3}, along with the corresponding reduced exciton mass and excitonic Bohr radius [8]. The lifetime measurements were carried out at 3.7 K [5, 6, 18].

a-Si:H experimental τ_R (s) $\approx 10^{-3}$ [5]						
E_{mx} (eV)	E_0 (eV)	μ_x / m_e	ε	a_x (nm)	R (s^{-1})	τ_R (s)
1.320	1.319	0.32(ii)-(iii)	12	2.0	13.94	71E-3
		3.55 (iv)		0.2	198.93	5E-3
a-As_2Se_3 experimental τ_R (s) $\approx 10^{-4}$ [18]						
1.100	1.1099	0.38 (ii)	8	1.11	1140	0.9E-3
		0.30 (iii)		1.41	554.6	1.8E-3
		3.05 (iv)		0.14	1.3×10^4	0.7E-4
a-As_2S_3 experimental τ_R (s) $\approx 10^{-4}$ [18]						
1.400	1.399	0.46 (ii)	5.8	0.67	4138.2	2.4E-4
		0.28 (iii)		1.10	9135.7	1E-3
		1.66 (iv)		0.18	3521.4	1E-4
a-Se experimental τ_R (s) $\approx 10^{-3}$ [18]						
0.740	0.739	0.47 (ii)	6.5	0.73	6093.3	1.6E-4
		0.35(iii)		0.98	2519.2	4E-4
		3.02 (iv)		0.11	77786.3	0.1E-4

For the inorganic amorphous semiconductors considered here, the calculated rates given in table 2 agree quite well with the experimental results, except in a-Se. The case of a-Se is somewhat different and the triplet PL occurs at a much lower energy of 0.74 eV with a Stokes shift of 1.46 eV. This gives a much smaller exciton Bohr radius in this material and hence a larger rate of spontaneous emission and a shorter theoretical radiative lifetime. It may also be noted that this material may be regarded to have the strongest charge carrier-phonon interaction. It is therefore possible that when both the carriers have relaxed to the tail states they recombine non-radiatively without giving any PL from the possibility (iv). Therefore, the only possible channels of the radiative recombination in this material may be through the possibilities (ii) and (iii), which give a theoretical radiative lifetime of a fraction of a millisecond, in reasonable agreement with the ms time range measured experimentally. Thus, the applicability of considering $|r| = a_x$ is apparently very reasonable in these materials.

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