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Kinematics of Exciton-Exciton Annihilation in Molecular Crystals

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A theory is developed for calculating the kinematic part of the exciton-exciton annihilation rate in molecular crystals. The spatial and spin motion of the excitons, as well as the annihilation process itself, is treated phenomenologically. Exciton propagation is assumed to take place as in the hopping model. The importance of the dimensionality of the exciton motion is pointed out; in nearly one- or two-dimensional cases, certain lifetime processes control the exciton collision rate, in contrast to the three-dimensional case. These lifetime processes include motion out of the one- or two-dimensional subspace and, for excitons with spin, spin relaxation. The theory leads to a description of magnetic field effects on the annihilation rate of triplet excitons at room temperature. When applied to triplet excitons in anthracene, this description gives a satsfactory fit to the observed effects and leads to the determination of the nearest-neighbor exciton annihilation rate, the singlet-channel annihilation rate constant, and the exciton diffusion constant for motion perpendicular to the *ab* plane of anthracene.

I. INTRODUCTION

Mutual annihilation of excitons in organic crystals is a well-established phenomenon. Its existence for singlet excitons was conjectured as early as 1958 by Northrop and Simpson[1] in an attempt to interpret photoconductivity in anthracene and has been invoked for this purpose by many workers since then.[2,3] Although the mechanism of exciton annihilation as a means of charge carrier generation is open to question,[4] the presence of the annihilation process for singlet excitons in anthracene has been demonstrated.[5] The evidence for the occurrence of mutual annihilation of triplet excitons in naphthalene and phenanthrene, in the form of observation of delayed fluorescence, dates back equally far,[6] although the interpretation in terms of mutual annihilation was suggested later.[7,8] Kepler *et al.*[9] presented conclusive evidence for explaining the delayed fluorescence in anthracene crystals in terms of triplet-triplet annihilation. Since then triplet-triplet annihilation has been verified by others in anthracene[10] and has been observed in pyrene,[11] naphthalene,[11,12] and a number of mixed crystals.[8,12,13] In recent years, triplet-triplet annihilation has become a productive tool for the study of the properties of triplet excitons, mainly in anthracene. A comprehensive review of this work may be found in the paper of Avakian and Merrifield.[14]

The annihilation process is conventionally described by the equation

$$\frac{\partial}{\partial t}n(\mathbf{r},t)=-\gamma n(\mathbf{r},t)^2\,, \tag{1}$$

where $n(\mathbf{r},t)$ is the exciton density at the point $\mathbf{r}$ at time t. The pairwise annihilation mechanism implicit in (1) is applicable so long as the exciton density is small compared to the molecular density of the solid.

Two rate-determining processes govern the magnitude of γ: (a) the migration of the two excitons toward (as well as away from) one another, and (b) the annihilation of the two excitons once they are sufficiently close to interact.

In the present paper, we address ourselves only to process (a), treating (b) phenomenologically by means of an adjustable parameter. Theoretical efforts[2,8,15,16] at calculating the rate of process (b) have not resulted in reliable estimates of this rate, with perhaps the greatest source of uncertainty being the final density of states in this process.

Although expressions for γ in the present theory will involve the unknown rate constant of process (b), they are not devoid of experimental testability. Process (a) clearly determines an upper limit on γ, which may even

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be a good estimate of γ if annihilation of two adjacent excitons is sufficiently fast. For triplet excitons, it is possible to vary rate (b) by means of a magnetic field.[17] The resulting magnetic field dependence of γ depends on both processes (a) and (b). Measurements of this dependence can therefore be used to test any theory describing process (a) as well as to determine the rate constant of process (b). The present theory will be irrelevant for situations in which process (a) is fast compared to process (b), since γ is then entirely dependent on the latter process. This state of affairs has been assumed, without justification, in the theories of singlet-singlet annihilation.[2] The measured value of γ for singlet-singlet annihilation in anthracene, however, contradicts this assumption.[5] Measurements of γ for triplet-triplet annihilation indicate that processes (a) and (b) occur at comparable rates.[18] Accordingly, it appears that a theory of process (a) is relevant to all known cases of exciton-exciton annihilation in organic crystals.

The most primitive estimate of γ for conditions such that process (a) constitutes the rate-determining step in the annihilation scheme was given by Jortner *et al.*[15] based on a hopping model of exciton motion and the assumption that annihilation occurs whenever two excitons are on nearest-neighbor lattice sites; it is

$$\gamma \sim Z/\tau_1 N\,, \tag{2}$$

where Z is the number of nearest neighbors, τ_1 is the hopping time, and N is the number of molecules per unit volume. Implicit in this estimate is the assumption that excitons are distributed independently of one another so that the probability that a given exciton lands on a site neighboring another exciton after a single jump is simply Zn/N, where n is the exciton density. It is not hard to see that this assumption cannot be correct when the near-neighbor annihilation rate is fast compared to the jump rate. The annihilation process must in the steady-state limit lead to a correlation "hole" surrounding each exciton: The probability that an exciton is found one lattice spacing away from another exciton must be small compared to the uncorrelated probability n/N; for larger exciton separations, this probability can approach the uncorrelated value only gradually. Another estimate of γ, which does take into account the exciton-exciton correlation, has also been given by Jortner *et al.*,[15]

$$\gamma = 8\pi D R\,, \tag{3}$$

where D is the macroscopic exciton diffusion constant and R is an average lattice spacing. As before, rapid annihilation of excitons on nearest-neighbor sites has been assumed. The assumption of a hopping model of exciton motion is also implicit in (3), as pointed out by Kepler and Switendick.[19] What has not been recognized is that formula (3), taken from Smoluchowski's theory of coagulation,[20] is applicable only to three-dimensional systems, and that a qualitatively different expression results in systems where the exciton motion is essentially two- or one-dimensional. The qualitative difference between three-dimensional motion on the one hand and one- or two-dimensional motion on the other is perhaps most dramatically illustrated by the following result in the theory of the random walk[21]: A particle executing a random walk in one or two dimensions returns infinitely often to its initial position; in three dimensions, the probability that it ever returns is only about 0.35. Thus two excitons undergoing three-dimensional motion in an infinite crystal collide essentially only once, but if their motion is one- or two-dimensional, they collide repeatedly, the total number of collisions being determined by the lifetime of the excitons. We shall see that certain lifetime processes are as important as the diffusion constant D in determining the annihilation rate in one- or two-dimensional systems. This fact is significant because in most of the systems in which the annihilation process has been treated theoretically, namely, for triplet excitons in anthracene,[15,16] naphthalene,[15,16] and tetracene,[16] exciton motion was predicted to be confined largely to the *ab* plane. Recently, the nearly two-dimensional motion of triplet excitons in anthracene has been verified experimentally as well.[22] The usage of (3) in these systems, using for D an average of the anisotropic diffusion tensor,[15,16] is simply incorrect.

To evaluate γ in cases where the annihilation rate of two nearby excitons is comparable in magnitude to the rate at which excitons collide, the following scheme has been used[15,16]:

$$T+T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (TT) \xrightarrow{k_2} S\,, \tag{4}$$

where T is an "isolated" triplet exciton, (TT) is a pair of excitons sufficiently close that annihilation can take place, and S is a state in which the pair has disappeared. A modification of this scheme has been used by Merrifield[18,23] to explain some of the magnetic field experiments. The expression for γ becomes

$$\gamma = \frac{k_1}{1+k_{-1}/k_2}. \tag{5}$$

The parameter k_1, defined as the rate of change of

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density of close pairs per *squared* density of isolated excitons, has dimensions of rate × volume.

In the above scheme, the detailed motion of the annihilating exciton pair has been approximated by two simple transition processes: the formation and dissociation of a kind of compound exciton. To what extent such an approximation can be made and how the parameters k_1 and k_{-1} depend on parameters characterizing site-to-site exciton motion is the main subject of the present paper. It will be shown that in many cases an approximate expression for γ can indeed be cast into the form (5), so that in these cases more precise meaning can be assigned to k_1 and k_{-1}. It will also be shown, for certain aspects of the magnetic field dependence of triplet-triplet annihilation, that the simple kinetic scheme (4) must not be taken literally.

The present paper will endeavor to solve the kinematics of the annihilating exciton pair in detail, using dynamical quantities such as the exciton propagation and annihilation rates merely as known or adjustable parameters. Evaluations will be performed both in a continuum approximation, where excitons are treated as point particles satisfying a diffusion equation, and in the hopping model approximation for exciton motion. The band model of exciton motion will be bypassed, as it does not appear to be relevant to known cases of exciton-exciton annihilation at room temperature, while exhibiting considerably more complex kinematics. For triplet excitons, kinematics includes the spin motion in addition to spatial motion. Again, dynamical quantities such as the spin Hamiltonian will be used phenomenologically, with emphasis on the solution of the equations of motion. The theory will be compared with measurements of triplet-triplet annihilation in anthracene in the presence of a magnetic field.

II. CONTINUUM MODEL

We begin our treatment of exciton-exciton annihilation with a simple classical model in which spin degrees of freedom are ignored, and excitons are treated as point particles obeying an isotropic diffusion equation. This model enables us to obtain exact analytic results and yet turns out to be a good approximation to a more precise quantum-mechanical solution in many cases.

The model is similar to the model used by Smoluchowski in his theory of coagulation.[20] Smoluchowski considered a function $w(\mathbf{r},t)$ giving the probability density at time t, for a particle existing at a separation $\mathbf{r}$ from another particle, assumed fixed in space. He allowed $w(\mathbf{r},t)$ to satisfy a time-dependent diffusion equation with the boundary condition $w(\mathbf{r},t)=0$ on the surface of a sphere of radius R, and with the initial condition $w(\mathbf{r},0)=n$. The rate of coagulation was then computed from the net flux of particles into the sphere in the limit $t\rightarrow\infty$.

Smoluchoswki's procedure simply does not work in a one- or two-dimensional system: The particle flux approaches zero as $t\rightarrow\infty$ for the conditions stated. A further potential difficulty in his method is that the depletion of the diffusing particles due to coagulation with other particles of the system is not taken into account. Finally, we wish to improve on his boundary condition by allowing particles to coagulate (annihilate) at a finite rate.

We consider, instead of the function w, the two-particle distribution function $f_2(\mathbf{r}_1,\mathbf{r}_2,t)$ giving the probability density for finding a pair of excitons at $\mathbf{r}_1$ and $\mathbf{r}_2$. For a system with uniform exciton density $n(t)$, this function is only a function of $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, and we denote it by $f(\mathbf{r},t)$. We allow the bimolecular annihilation to proceed at a finite rate $\lambda(\mathbf{r})$ for two excitons separated by $\mathbf{r}$. We also include a unimolecular decay term describing the decay of excitons at a rate β. Finally, in order to achieve a steady-state solution, we include a uniform source term which produces excitons randomly at a rate α per unit volume.

The complete equation for $f(\mathbf{r},t)$ is derived in Appendix A. For isotropic diffusion it is

$$\frac{\partial}{\partial t}f(\mathbf{r},t)=2\alpha n(t)-2\beta f(\mathbf{r},t)+2D\nabla^2 f(\mathbf{r},t)-\lambda(\mathbf{r})f(\mathbf{r},t)-\int d\mathbf{r}'\,[\lambda(\mathbf{r}'-\mathbf{r})+\lambda(\mathbf{r}')]g(\mathbf{r},\mathbf{r}',t)\,,\quad(6)$$

where D is the exciton diffusion constant and $g(\mathbf{r},\mathbf{r}',t)$ is a three-exciton distribution function giving the probability density for finding three excitons, one at some arbitrary point $\mathbf{r}_0$, the others at $\mathbf{r}_0+\mathbf{r}$, $\mathbf{r}_0+\mathbf{r}'$. The term involving g describes the destruction of the original pair by background particles and was omitted by Smoluchowski. This term would lead to $f(\mathbf{r},t)\rightarrow 0$ as $t\rightarrow\infty$ when sources are absent, even when there is no unimolecular decay, and even in three dimensions. With sources present, but without the unimolecular decay term, the background term in fact determines the annihilation rate in one- or two-dimensional systems, even for arbitrarily dilute exciton concentrations. This term can only be neglected when the steady-state exciton concentration is determined by the unimolecular decay rate, i.e., for exciton densities such that bimolecular annihilation is negligible compared to unimolecular decay.

The time development of the exciton density is also derived in Appendix A [it is not directly derivable from (6)]:

$$\frac{\partial}{\partial t}n(t)=\alpha-\beta n(t)-\int d\mathbf{r}\,\lambda(\mathbf{r})f(\mathbf{r},t)\,.\quad(7)$$

We solve (6) and (7) in the steady-state limit. We assume that the equilibrium density is indeed sufficiently low that bimolecular annihilation terms can be neglected in comparison to the decay terms. If this is not the case, we are faced with the evaluation of the three-particle function, whose equation of motion will involve a four-particle distribution function, etc. Even if we make a suitable approximation for g, we will find that in general the bimolecular annihilation will not be proportional to the square of the density. In the low-density limit, however, we have simply (at equilibrium) $\alpha=\beta n$. Then (6) reduces to

$$0=2\beta[n^2-f(\mathbf{r})]+2D\nabla^2 f(\mathbf{r})-\lambda(\mathbf{r})f(\mathbf{r}). \tag{8}$$

The last equation implies that $f(\mathbf{r})$ is proportional to n^2 [assuming $\lambda(\mathbf{r})\rightarrow 0$ as $r\rightarrow\infty$] if it is to remain finite as $r\rightarrow\infty$. Thus with the aid of (6), we see that the law (1) is obeyed, with γ given by

$$\gamma=n^{-2}\int\lambda(\mathbf{r})f(\mathbf{r})\,d\mathbf{r}. \tag{9}$$

Next, we specialize the model further as follows: We introduce the boundary $r=R$; for $r>R$, $\lambda(\mathbf{r})$ vanishes, while for $r<R$ it is uniform, $\lambda(\mathbf{r})=\lambda$. We furthermore assume that the diffusion constant is infinite for $r<R$. The last condition implies a uniform density inside the boundary. Insofar as this continuum model is to represent nearest-neighbor annihilation in the hopping model of exciton motion, R is to be taken as an average lattice spacing; the portion of the distribution function contained inside $r<R$ represents excitons situated on nearest-neighbor sites. We can even mock up the exclusion principle in this model by excluding a volume $r<R_0$ so as to represent the impossibility of two excitons occupying the same lattice site. This is done via the boundary condition that the gradient of f be zero at $r=R_0$ and is equivalent to a constant distribution function occupying the region $R_0<r<R$. We shall denote by v the volume (respectively, area or length) of the appropriate region so occupied.

The solution of (8) under the above conditions is, for $r>R$,

$$f(r)=n^2+\tfrac{1}{2}\lambda v n^2 g(r)\Big/\left(1+\beta\int_0^R d\mathbf{r}'\,g(r')-(\beta+\tfrac{1}{2}\lambda)vg(R)\right), \tag{10}$$

where $g(r)$ is the Green's function for the diffusion equation, i.e.,

$$\delta(\mathbf{r})=D\nabla^2 g(r)-\beta g(r). \tag{11}$$

For $r<R$, the solution is the constant equal to $f(R)$ for the exterior solution. The rate constant $\gamma=n^{-2}\lambda v f(R)$ can be written in the form

$$\gamma=\frac{\gamma_\infty}{1+\gamma_\infty/\lambda v}, \tag{12}$$

TABLE I. Maximum annihilation rates in continuum model. Units of listed quantities depend on dimensionality; $g(r)$ has units of density times time, γ has units of reciprocal density times reciprocal time. The values for γ_∞ are valid only in the limit $(\beta/D)^{1/2}\gg R$. K_0 is the modified Bessel function for imaginary argument.

Dimensions	$g(r)$	γ_∞
1	$-\{\exp[-(\beta/D)^{1/2}r]\}/2(D\beta)^{1/2}$	$4(D\beta)^{1/2}$
2	$-K_0[(\beta/D)^{1/2}r]/2\pi D$	$-4\pi D/\{\ln[\frac{1}{2}(\beta/D)^{1/2}R]+0.577\cdots\}$
3	$-\{\exp[-(\beta/D)^{1/2}r]\}/4\pi Dr$	$8\pi DR[1+(\beta/D)^{1/2}R]$

where

$$\gamma_\infty=-2\left(1+\beta\int_0^R d\mathbf{r}'\,g(r')-\beta vg(R)\right)\Big/g(R) \tag{13}$$

is the rate constant in the diffusion-controlled limit $\lambda\rightarrow\infty$. The result (12) is indeed in the form (5), with $k_1=\gamma_\infty$, $k_{-1}/k_2=\gamma_\infty/\lambda v$; there is no basis for assigning separate values for k_{-1} and k_2.

Table I summarizes the expressions for $g(r)$ in various dimensions. Also given are approximate expressions for γ_∞ in the limit $R\ll L$, where L is the diffusion length $L=(D/\beta)^{1/2}$. It is clear from this table that β can be ignored in a three-dimensional system (provided $R\ll L$) but never in a one- or two-dimensional system. The expressions for γ_∞ are valid only when unimolecular decay dominates bimolecular annihilation [otherwise the basic law (1) fails and γ becomes meaningless].

The results of the continuum model are meant primarily to illustrate the effects of dimensionality. We have not discussed intermediate cases of anisotropic diffusion partly because they are not amenable to simple solution (except for artificial boundary shapes) and partly because such cases are best handled by the theory of the next sections, in which exciton motion is dealt with more rigorously.

III. SINGLET EXCITONS IN HOPPING MODEL

A. General Solution

In a quantum-mechanical treatment of exciton motion the classical distribution functions are replaced by density matrices. In the present paper, we confine attention to systems in which exciton motion can be described by means of the so-called hopping model. In this model, valid whenever the exciton mean free path is small compared to a lattice spacing, the exciton density matrix is diagonal in the spatial indices[24] and can be represented as a function of position $\rho(\mathbf{R})$, where $\mathbf{R}$ denotes a lattice point. We write the equation of motion for this single-exciton density matrix in the

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[24] P. Avakian, V. Ern, R. E. Merrifield, and A. Suna, Phys. Rev. **165**, 974 (1968).

form

$$\frac{\partial}{\partial t}\rho(\mathbf{R},t)=\sum_{\mathbf{R}'}\Psi(\mathbf{R}-\mathbf{R}')\rho(\mathbf{R}',t)-\rho(\mathbf{R},t)\sum_{\mathbf{R}'}\Psi(\mathbf{R}')-\beta\rho(\mathbf{R},t)+\alpha, \quad (14)$$

where $\Psi(\mathbf{R})$ is the incoherent jump rate for an exciton hopping by a lattice vector $\mathbf{R}$. The two-particle diagonal density matrix will for a uniform system depend only on the vector difference of the positions of the two excitons and will be denoted by $\rho_2(\mathbf{R})$ where $\mathbf{R}$ is this vector difference. It satisfies an equation analogous to (6), derived in Appendix B. We pass directly to the steady-state equation in the limit when bimolecular annihilation is negligible compared to unimolecular decay, the equation analogous to (8):

$$0=2\beta[(nv)^2-\rho_2(\mathbf{R})]+2\sum_{\mathbf{R}'}\Psi(\mathbf{R}-\mathbf{R}')\rho_2(\mathbf{R}')-2\rho_2(\mathbf{R})[\sum_{\mathbf{R}'}\Psi(\mathbf{R}')-\Psi(\mathbf{R})]-\lambda(\mathbf{R})\rho_2(\mathbf{R}). \quad (15\text{a})$$

Here v denotes the average volume per molecule of the crystal, i.e., nv is just the probability that an exciton is found on any given molecule. The quantity $\lambda(\mathbf{R})$ is the phenomenological annihilation rate for a pair of excitons separated by $\mathbf{R}$. It has been assumed that $\lambda(\mathbf{R})$ is small compared to the exciton scattering rate, so that the annihilation process does not mix in spatially off-diagonal elements of the density matrix. Equation (15a) holds only for $\mathbf{R}\neq 0$. For $\mathbf{R}=0$ the exclusion principle imposes the condition

$$\rho_2(0)=0. \quad (15\text{b})$$

Equation (15a), together with the condition (15b), is formally "solved" by the expression

$$\rho_2(\mathbf{R})=(nv)^2+g(\mathbf{R})[\sum_{\mathbf{R}'}\Psi(\mathbf{R}')\rho_2(\mathbf{R}')+\beta(nv)^2]+\sum_{\mathbf{R}'}g(\mathbf{R}-\mathbf{R}')[\tfrac{1}{2}\lambda(\mathbf{R}')\rho_2(\mathbf{R}')-\Psi(\mathbf{R}')\rho_2(\mathbf{R}')], \quad (16)$$

where $g(\mathbf{R})$ is the Green's function satisfying

$$\delta_{\mathbf{R},0}=\sum_{\mathbf{R}'}\Psi(\mathbf{R}-\mathbf{R}')g(\mathbf{R}')-g(\mathbf{R})\sum_{\mathbf{R}'}\Psi(\mathbf{R}')-\beta g(\mathbf{R})$$

$$(\delta_{\mathbf{R},0}=0 \quad \text{for } \mathbf{R}\neq 0,\quad \delta_{0,0}=1). \quad (17)$$

The expression (16) is useful whenever the parameters $\Psi(\mathbf{R})$ and $\lambda(\mathbf{R})$ are nonzero for only a finite number, say p, of lattice vectors. Then (16) reduces to a finite set of p equations in the p unknowns $\rho_2(\mathbf{R})$ for $\mathbf{R}$ such that either $\lambda(\mathbf{R})\neq 0$ or $\Psi(\mathbf{R})\neq 0$, provided, of course, that $g(\mathbf{R})$ is known. This is all the information we need for determining the annihilation rate per unit volume, given by (see Appendix B)

$$\gamma n^2=v^{-1}\sum_{\mathbf{R}'}\lambda(\mathbf{R}')\rho_2(\mathbf{R}'). \quad (18)$$

B. Smooth Approximation

In order to get explicit analytical results, we resort to a procedure we henceforth call the "smooth approximation." We assume that both $g(\mathbf{R})$ and $\rho_2(\mathbf{R})$ do not vary much over those values of $\mathbf{R}$ for which either $\lambda(\mathbf{R})$ or $\Psi(\mathbf{R})$ is nonvanishing and, in fact, replace them by the constants $g(\bar{R})$ and $\rho_2(\bar{R})$ for all such $\mathbf{R}$. This procedure is exact for the simple cubic, the square, and the uniform one-dimensional lattices when $\lambda(\mathbf{R})$ and $\Psi(\mathbf{R})$ are nonzero for one lattice spacing only. In general, it is expected to be valid whenever nearest-neighbor jump and annihilation rates dominate and are nearly isotropic, while the diffusion length is large compared to a lattice spacing. In the smooth approximation, Eqs. (16)–(18) become, for $\mathbf{R}=0$,

$$0=(nv)^2+g(0)[\Psi\rho_2(\bar{R})+\beta(nv)^2]+g(\bar{R})[\tfrac{1}{2}\lambda\rho_2(\bar{R})-\Psi\rho_2(\bar{R})], \quad (19)$$

$$1=\Psi[g(\bar{R})-g(0)]-\beta g(0), \quad (20)$$

$$\gamma n^2=v^{-1}\lambda\rho_2(\bar{R}), \quad (21)$$

where

$$\lambda=\sum_{\mathbf{R}'}\lambda(\mathbf{R}'),\quad \Psi=\sum_{\mathbf{R}'}\Psi(\mathbf{R}').$$

Solving for $\rho_2(\bar{R})$ we find that γ may be cast into precisely the form (12), where

$$\gamma_\infty=-2v[1+\beta g(0)]/g(\bar{R}) \quad (22)$$

and where v now stands for the volume per molecule of the crystal.

This result is essentially the same as the continuum result (13). Even the discrete Green's functions may be approximated by the continuum Green's functions, as follows. As is well known, the hopping equation [Eq. (17)] may be approximated by a diffusion equation with a diffusion tensor given by

$$D_{ij}=\tfrac{1}{2}\sum_{\mathbf{R}}\Psi(\mathbf{R})R_iR_j, \quad (23)$$

provided the solution is smooth on the scale of a lattice spacing. Then, for isotropic diffusion, Eq. (17) is the same as Eq. (11), except for a factor v in the source term [the Kronecker δ function of (17) is equivalent to $v\delta(\mathbf{r})$ in the continuum limit]. Whether or not the discrete Green's function may be approximated by the continuous one in the expression for γ depends on whether or not the smoothness criterion holds for g evaluated at one lattice spacing. From Table I we see that in both one and two dimensions $g(r)$ may be made arbitrarily smooth by making the diffusion length $(D/\beta)^{1/2}$ sufficiently large compared to a lattice spacing. In three dimensions, smoothness is achieved only for large r, and the continuum approximation cannot be expected to give γ very accurately. Except for this reservation, the expressions for γ_∞ given in Table I will then be applicable in the discrete calculation as well, provided the assumptions of the "smooth approximation" are valid.

C. Nearly Two-Dimensional Case

As an important example for which the smooth approximation fails we consider a model of nearly two-dimensional exciton motion. We imagine the crystal in this case as a stack of parallel planes such that exciton motion within each plane is rapid compared to the rate of transfer between planes. Let us suppose that the diffusion length for intraplanar motion is large compared to a lattice spacing so that this motion can be described by a continuum diffusion equation, with a diffusion constant D. Interplanar motion will be characterized via a jump rate Ψ between neighboring planes. The annihilation rate will depend on the Green's function for diffusion in this system, whose equation is

$$\delta(\mathbf{r})\delta_{n0}=D\nabla^2 g_n(\mathbf{r})+\Psi[g_{n+1}(\mathbf{r})+g_{n-1}(\mathbf{r})]-(2\Psi+\beta)g_n(\mathbf{r}). \quad (24)$$

Here $\mathbf{r}$ is a continuous two-dimensional vector and n labels the planes between which the hopping-type motion is occurring. Equation (24), with the condition $g_n(\mathbf{r})\rightarrow 0$ when $r\rightarrow\infty$ or $n\rightarrow\infty$, is solved by

$$g_n(r)=-(2\pi D)^{-1}(-1)^n K_n\{\tfrac{1}{2}r[(4\Psi/D+\beta/D)^{1/2}+(\beta/D)^{1/2}]\}I_n\{\tfrac{1}{2}r[(4\Psi/D+\beta/D)^{1/2}-(\beta/D)^{1/2}]\}, \quad (25)$$

where K_n and I_n are Bessel functions as defined in Watson's treatise.[25]

This solution tells us all we want to know about the nearly two-dimensional motion; it is not necessary to compute γ, except to keep in mind that γ is determined by $g_n(r)$ evaluated at essentially one lattice parameter from the origin. For small arguments we may expand the Bessel functions in terms of their well-known series. A sufficient condition for the validity of this expansion is

$$r[(\beta+2\Psi)/D]^{1/2}\ll 1. \quad (26)$$

For r approximately equal to one lattice spacing this criterion is essentially the requirement that the rate of depletion of excitons from a given lattice site, due to either decay or out-of-plane diffusion, be small compared to the in-plane jump rate. When (26) holds, the logarithmic dependence of K_0 for small r leads to $g_0(r)\gg g_1(r)$, so that the motion can be indeed approximated as being two-dimensional. To be sure, the Green's function $g_0(r)$ for in-plane diffusion is approximated by the true two-dimensional Green's function (see Table I) only for small r {for large r it approaches the three-dimensional behavior $g_0(r)\sim\exp[-r(\beta/D)^{1/2}]/r$}; but small r is all that matters in the calculation of γ.

We thus have the expected result that the exciton-exciton annihilation rate for excitons undergoing nearly two-dimensional diffusion can indeed be calculated by means of a two-dimensional theory. The result (25) shows, however, that out-of-plane diffusion has a non-negligible effect on this two-dimensional theory: Although for small r a two-dimensional diffusion equation correctly describes the problem, the exciton decay rate is altered. The effective decay rate is now

$$\beta_{\mathrm{eff}}=\{\tfrac{1}{2}[(4\Psi+\beta)^{1/2}+\beta^{1/2}]\}^2=\Psi+\tfrac{1}{2}\beta+(\Psi\beta+\tfrac{1}{4}\beta^2)^{1/2}. \quad (27)$$

The decay rate has become enhanced by the presence of the out-of-plane motion, such motion in effect providing a sink for excitons. We expect a similar enhancement of the decay rate in the case of nearly one-dimensional motion, provided the excitons can move out of the line of primary motion in two independent directions. Although we do not have an explicit model to back up this assertion, it is clear from the general theorem on the probabilities of return to the origin that only three-dimensional motion can act to effectively remove particles from any given point.

IV. TRIPLET EXCITONS

A. General Remarks

The theory of annihilation of triplet excitons involves additional complexity because the annihilation rate is expected to depend on the total spin angular momentum of the annihilating pair. As a result, the spin degrees of freedom of the annihilating exciton pair must be explicitly taken into account. We shall restrict our theory to cases where a hopping model of exciton motion is applicable, and deal as before with the spatially diagonal exciton pair density matrix $\rho_2(\mathbf{R})$ where this quantity is now a matrix in the spin degrees of freedom. As we shall see, the spin relaxation rate is generally slow compared to hopping and annihilation rates, so that we will have to deal with the full spin matrix.

The rate of change of the pair density matrix due to exciton-exciton annihilation will be given by a matrix relation of the form (see Appendix B)

$$\left(\frac{\partial}{\partial t}\right)_{\mathrm{ann}}\rho_2(\mathbf{R})=-\tfrac{1}{2}[\Lambda(\mathbf{R})\rho_2(\mathbf{R})+\rho_2(\mathbf{R})\Lambda(\mathbf{R})], \quad (28)$$

where $\Lambda(\mathbf{R})$ is a matrix in the spin indices.

It has been assumed as before that the annihilation rate is slow compared to the exciton scattering rate, so that the matrix Λ is diagonal in the spatial indices. We expect the spin dependence of Λ for triplet excitons to have the form

$$\Lambda(\mathbf{R})=\lambda_S(\mathbf{R})P_S+\lambda_T(\mathbf{R})P_T+\lambda_Q(\mathbf{R})P_Q, \quad (29)$$

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[25] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1958).

where P_S, P_T, and P_Q are, respectively, projection operators into the singlet, the triplet, and the quintet manifolds of pair states; the scalar quantities λ_S, λ_T, and λ_Q are the corresponding rates of pair annihilation. In practice, we shall always neglect λ_Q, as there is no known system where double the triplet exciton energy even remotely approaches the estimated energy of the lowest quintet state.

It now also becomes meaningful to speak of the annihilation rate via the singlet (triplet, quintet) channel. To some extent, such a separation of annihilation rates can be accomplished experimentally—e.g., the delayed fluorescence observed in anthracene as a result of exciton-exciton annihilations comes primarily from the singlet channel, since the emission is from a singlet state.

The annihilation rate in any given channel will now also depend on the removal of excitons from that channel via spin relaxation, which tends to equalize the populations of all spin states. This fact will have a profound effect on annihilation in one- and two-dimensional systems if the spin relaxation rate is large compared to the effective decay rate. In a three-dimensional system spin relaxation will be important only if its rate is comparable to the exciton hopping rate, a case we do not consider in this paper.

B. Annihilation Rate in Absence of Spin Relaxation

The calculation of the annihilation rate constant γ is considerably simpler in cases when spin relaxation can be neglected. Such cases include all systems where exciton diffusion is three dimensional and roughly isotropic (with the usual proviso that spin relaxation rates be slow compared to hopping rates). For one- and two-dimensional systems, this theory will apply only if the net effective decay rate is large compared to the spin relaxation rate.

The matrix equation of motion for the pair density matrix now has the form (in the steady-state limit)

$$\begin{aligned}0=-i[\mathcal{H}(\mathbf{R}),\rho_2(\mathbf{R})]+2\beta[(\tfrac{1}{3}nv)^2\mathbf{1}-\rho_2(\mathbf{R})]\\+2\sum_{\mathbf{R}'}\Psi(\mathbf{R}-\mathbf{R}')\rho_2(\mathbf{R}')-2\rho_2(\mathbf{R})[\sum_{\mathbf{R}'}\Psi(\mathbf{R}')-\Psi(\mathbf{R})]\\-\tfrac{1}{2}[\Lambda(\mathbf{R})\rho_2(\mathbf{R})+\rho_2(\mathbf{R})\Lambda(\mathbf{R})],\end{aligned}\quad(30)$$

where $\mathcal{H}(\mathbf{R})$ is the exciton spin Hamiltonian (we have set $\hbar=1$). We have assumed that this Hamiltonian is a function only of the exciton separation, i.e., that the single-exciton spin Hamiltonian is spatially uniform. This assumption should be valid whenever the exciton hopping rate is rapid compared to the spin relaxation rate, for then the moving exciton will experience the average of the spin Hamiltonians associated with possibly inequivalent crystal sites.[26] We have also assumed that excitons are introduced in all possible spin states with equal probability (source proportional to the unit matrix $\mathbf{1}$). This assumption will be applicable only at temperatures such that at equilibrium all spin states are essentially equally populated. Then the only further requirement is that the spin relaxation time be short compared to the lifetime of the excitons; this will assure the smoothing out of nonuniformities in spin state populations introduced by the exciton creation process. We have ignored any dependence of the hopping rates $\Psi(\mathbf{R})$ on the exciton separation, in effect neglecting attractive or repulsive exciton-exciton interactions. We shall see that this assumption does not lead to serious errors in the theory, provided only that the interaction is short range and small compared to the annihilation rate, in appropriate units.

With spin relaxation neglected, the calculation of the annihilation rate in the triplet channel can be neatly separated out.[23] This circumstance is due to the fact that triplet total spin states of a pair of triplet excitons are odd under exchange of particles, whereas the singlet and quintet states are even. Any odd spin state must be a triplet, so that the projection operator P_T is equal to the projection operator into the manifold of odd states; within this manifold $\Lambda(\mathbf{R})$ is the constant matrix $\lambda_T(\mathbf{R})\mathbf{1}$. Since $\mathcal{H}(\mathbf{R})$ must be even under interchange of particles it does not mix even and odd states, either. The result is that the odd-odd matrix elements of (30) involve only the odd-odd matrix elements of $\rho_2(\mathbf{R})$. The total annihilation rate of pairs in the triplet channel will be (see Appendix B)

$$\gamma_T n^2=\tfrac{1}{2}v^{-1}\sum_{\mathbf{R}}\lambda_T(\mathbf{R})\ \mathrm{Tr}[\rho_2(\mathbf{R})]_{\mathrm{odd}},\quad(31)$$

where the trace is to be performed over only that part of $\rho_2(\mathbf{R})$ which has matrix elements between odd spin states. It has been assumed that each annihilation event results in the destruction of only one triplet exciton.

By performing the trace over the odd part of Eq. (30), we observe that $\mathrm{Tr}[\rho_2(\mathbf{R})]_{\mathrm{odd}}$ satisfies an equation of precisely the same form as of that satisfied by $\rho_2(\mathbf{R})$ in the spinless case [Eq. (15a)], except that the source term is now $\frac{1}{3}(nv)^2$. The methods of solution of the spinless case can then be applied; within the smooth approximation, the annihilation rate constant γ_T is given by

$$\gamma_T=\frac{\frac{1}{6}v\lambda_T}{1-\frac{1}{2}\lambda_T g(\bar{R})/[1+\beta g(0)]}.\quad(32)$$

The separation of Eq. (30) into odd and even parts also simplifies the calculation of the singlet-channel annihilation rate. We can no longer eliminate the spin degree of freedom, however, since the spin Hamiltonian will provide for a mixing of singlet and quintet states, whereas annihilation will be assumed to occur for singlet states only.

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[26] H. Sternlicht and H. M. McConnell, J. Chem. Phys. **35**, 1793 (1961).

Let us take a closer look at this spin Hamiltonian, and write it in the form

$$\mathcal{H}(\mathbf{R})=\mathcal{H}+V(\mathbf{R}), \tag{33}$$

where $\mathcal{H}$ is a matrix independent of $\mathbf{R}$ and consists of the sum of the single-exciton Hamiltonians for the two members of the exciton pair. $V(\mathbf{R})$ represents the exciton-exciton interaction term and is expected to be essentially the dipole-dipole interaction between the magnetic moments of the two triplet excitons.

We expect $V(\mathbf{R})$, for $\mathbf{R}$ connecting nearest-neighbor sites, to be at most comparable to $\mathcal{H}$, since $\mathcal{H}$, in the absence of external magnetic fields, arises from a similar dipolar interaction, though between electrons on the same molecule. The increased size of the latter interaction, due to smaller average separation between the electrons, is balanced by the factor $\frac{1}{4}$ due to the smaller spin of the electrons. Since a dipolar interaction decreases as R^{-3}, $V(\mathbf{R})$ should be negligible compared to $\mathcal{H}$ except for R of the order of a lattice spacing or two. This circumstance enables us to solve the equation of motion for $\rho_2(\mathbf{R})$ in terms of a Green's function which does not involve $V(\mathbf{R})$. Let us express (30) in a basis of even spin states $|l\rangle$ which diagonalize $\mathcal{H}$ with eigenvalues E_l; then

$$-i\langle l|[\mathcal{H},\rho_2(\mathbf{R})]|l'\rangle=-i[E_l-E_{l'}]\langle l|\rho_2(\mathbf{R})|l'\rangle. \tag{34}$$

This choice of basis uncouples the equations for the various matrix elements of $\rho_2(\mathbf{R})$, for large R, and leads us to define the complex Green's function $g(\mathbf{R},\,\beta+iE)$ satisfying

$$\delta_{\mathbf{R},0}=\sum_{\mathbf{R}'}\Psi(\mathbf{R}-\mathbf{R}')g(\mathbf{R}',\beta+iE)-g(\mathbf{R},\beta+iE)\sum_{\mathbf{R}'}\Psi(\mathbf{R}')$$
$$-(\beta+iE)g(\mathbf{R},\,\beta+iE). \tag{35}$$

Equation (30) is then formally solved as

$$\langle l|\rho_2(\mathbf{R})|l'\rangle=\delta_{ll'}(\tfrac{1}{3}nv)^2+g[\mathbf{R},\beta+\tfrac{1}{2}i(E_l-E_{l'})]$$
$$\times\{\sum_{\mathbf{R}'}[\Psi(\mathbf{R}')\langle l|\rho_2(\mathbf{R}')|l'\rangle]+\beta(\tfrac{1}{3}nv)^2\delta_{ll'}\}$$
$$+\sum_{\mathbf{R}'}g[\mathbf{R}-\mathbf{R}',\beta+\tfrac{1}{2}i(E_l-E_{l'})]\{-\Psi(\mathbf{R}')\langle l|\rho_2(\mathbf{R}')|l'\rangle$$
$$+\langle l|\tfrac{1}{4}[\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')]$$
$$-i\tfrac{1}{2}[V(\mathbf{R}'),\rho_2(\mathbf{R}')]|l'\rangle\}. \tag{36}$$

As in the spinless case, (36) reduces to a finite set of equations when $g(\mathbf{R},\,\beta+iE)$ is known and when the number of lattice vectors $\mathbf{R}$, such that $\Lambda(\mathbf{R})\neq 0$, $\Psi(\mathbf{R})\neq 0$, and now also $V(\mathbf{R})\neq 0$, is finite.

The circumstance that both $\Lambda(\mathbf{R})$ and $V(\mathbf{R})$ are short range will permit us to neglect $V(\mathbf{R})$ in most cases of interest, when the effect of $V(\mathbf{R})$ on the density matrix will be negligible compared to that of $\Lambda(\mathbf{R})$. As will be seen when specific numerical estimates are made of various quantities in the present theory, spin-spin interactions such as $V(\mathbf{R})$ and $\mathcal{H}$ are an order of magnitude smaller, in appropriate units, than the exciton hopping rate. The near-neighbor annihilation rate, on the other hand, must be comparable to or greater than the hopping rate if the exciton motion is to influence the annihilation rate in a nontrivial way. Thus this annihilation rate will in interesting cases be large compared to the spin-spin interaction, permitting the neglect of the latter. Note that by contrast the zero-field Hamiltonian $\mathcal{H}$ cannot be neglected compared to $\Lambda(\mathbf{R})$, because $\mathcal{H}$ has infinite range. In the following, the interaction $V(\mathbf{R})$ will be set equal to zero.

Within the smooth approximation,[illegible] and with $V(\mathbf{R})=0$, Eq. (36) becomes

$$\langle l|\rho_2(\bar{R})|l'\rangle=\delta_{ll'}(\tfrac{1}{3}nv)^2+\tfrac{1}{4}G[\beta+i\tfrac{1}{2}(E_l-E_{l'})]$$
$$\times\langle l|\Lambda\rho_2(\bar{R})+\rho_2(\bar{R})\Lambda|l'\rangle, \tag{37}$$

where the function G is defined as

$$G(\beta)=g(\bar{R},\beta)/[1+\beta g(0,\beta)] \tag{38}$$

and where

$$\Lambda=\sum_{\mathbf{R}}\Lambda(\mathbf{R}).$$

For $\Lambda=\lambda_S|S\rangle\langle S|$, (37) takes the form of Johnson and Merrifield's[23] Eq. (10), where the function G is in effect approximated via the relation

$$G(\beta+\tfrac{1}{2}iE)/G(\beta)\approx(1+iE/k_{-1})^{-1} \tag{39}$$

and where the parameter $k=k_2/k_{-1}$ is to be identified with the following combination of parameters in the present theory:

$$k=-\tfrac{1}{2}\lambda_S G(\beta). \tag{40}$$

Equation (37), for even pair states $|l\rangle$, represents a set of 21 equations for the 21 unknown matrix elements. It is possible to simplify this system, for $\Lambda=\lambda_S|S\rangle\langle S|$, to a system of only six equations in the six unknowns[27]:

$$A_l=(\tfrac{1}{3}nv)^{-2}\langle l|S\rangle\sum_{l'}\langle S|l'\rangle\langle l'|\rho_2(\mathbf{R})|l\rangle, \tag{41}$$

in terms of which the annihilation rate constant can be expressed as

$$\gamma_S=(\tfrac{1}{9}v\lambda_S)\sum_{l}A_l. \tag{42}$$

The equations satisfied by A_l are

$$\{1-\tfrac{1}{4}\lambda_S\sum_{l'}|\langle S|l'\rangle|^2G[\beta+i\tfrac{1}{2}(E_{l'}-E_l)]\}A_l$$
$$=|\langle S|l\rangle|^2\{1+\tfrac{1}{4}\lambda_S\sum_{l'}G[\beta+i\tfrac{1}{2}(E_{l'}-E_l)]A_{l'}^*\}. \tag{43}$$

Equation (43) can, in general, be solved only numerically. Certain special limits, as in the theory of Johnson and Merrifield,[23] are, however, analytically soluble and are of interest. One such limit occurs when all energy

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[27] R. E. Merrifield (private communication).

differences $E_l - E_{l'}$ are sufficiently large in magnitude that

$$G[\beta+\tfrac{1}{4}i(E_l-E_{l'})] \ll G(\beta), \quad l \neq l'. \tag{44}$$

In a three-dimensional system sufficient conditions for this to occur are that $|E_l - E_{l'}| \gg \Psi$ and $|E_l - E_{l'}| \gg \beta$; in one- or two-dimensional systems, however, because of the sensitive dependence of $g(\mathbf{R},\beta)$ on β, the condition $|E_l - E_{l'}| \gg \beta$ suffices.

When (44) holds, the pair density matrix becomes diagonal, and the theory of the annihilation rate constant becomes identical in form to that originally given by Merrifield.[18] The system of coupled equations, Eq. (43), decouples into equations for the quantities A_l, which now become real. From (42), the expression for γ is then found to be

$$\gamma_S = (\tfrac{1}{9}v\lambda_S) \sum_l |\langle S|l\rangle|^2 / [1+k|\langle S|l\rangle|^2], \tag{45}$$

where k is given in (40). For this case, the present theory in effect represents a theory of the parameter $k = k_2/k_{-1}$ as well as Merrifield's parameter k_1, which in (45) appears effectively as $k_1 = v\lambda_S/k = -2v/G(\beta)$.

The significance of (45) in interpreting the observed magnetic field effects on the triplet-triplet annihilation rate has been discussed in detail by Merrifield.[18] He showed, among other things, that the directional resonances, dips in the delayed fluorescence intensity for special orientations of an externally applied magnetic field, are a consequence of degeneracies occurring between two of the pair energy levels. The behavior of γ in the vicinity of one of these resonances can also be estimated via an explicitly soluble limit of (43), namely, one in which all but two pair energy levels, say, E_1 and E_2 are sufficiently far apart that (44) holds. The result for γ_S is a sum of the form (45), not including $l = 1, 2$, plus the term

$$\gamma_{12}(E) = \left(\frac{\lambda_S}{9v}\right) \frac{|\langle 1|S\rangle|^2 + |\langle 2|S\rangle|^2 + 2k|\langle 1|S\rangle\langle 2|S\rangle|^2[1-f(E)]}{1+k(|\langle 1|S\rangle|^2 + |\langle 2|S\rangle|^2) + k^2|\langle 1|S\rangle\langle 2|S\rangle|^2[1-f(E)]}, \tag{46}$$

where $E = E_1 - E_2$ and the function $f(E)$ is defined as

$$f(E) = \mathrm{Re}\left(\frac{G(\beta+i\frac{1}{2}E)[1+\frac{1}{2}k(|\langle 1|S\rangle|^2 + |\langle 2|S\rangle|^2)]}{G(\beta)+G(\beta+i\frac{1}{2}E)\frac{1}{2}k(|\langle 1|S\rangle|^2 + |\langle 2|S\rangle|^2)}\right). \tag{47}$$

This result is, of course, the same as in the theory of Johnson and Merrifield[23] if the approximation (39) is made. The function $f(E)$ determines the way in which γ varies between the on-resonance condition $[E=0, f(E)=1]$ and the off-resonance limit $[f(E) \rightarrow 0]$. The shape of the resonance, as a function of the direction of the external magnetic field (which determines E), is in the present theory predicted to be qualitatively different from the Lorentzian shape resulting from the approximation (39). Unfortunately, however, the fine details of the resonance shape may for a real crystal be smeared out by crystal imperfections, such that a Lorentzian shape may be a good approximation. In principle, the observed resonance shapes for a good crystal should yield information on exciton dynamics, such as the hopping rate and the effective decay rate β.

The present theory of line shapes constitutes in effect the theory of the pair dissociation rate parameter k_{-1} of the earlier theories, although, of course, an explicit expression for k_{-1} is meaningless in view of the fact that the resonance shapes as deduced from the diffusional motion of the excitons cannot be everywhere approximated by Lorentzians. One way of quantifying the new resonance shapes is to determine the half-width Γ of $\mathrm{Re}[G(\beta+\frac{1}{2}iE)]$; Eq. (39) then shows that $\Gamma = k_{-1}$ in the earlier theories, so that it may be regarded as an approximation to k_{-1}. Explicit expressions for Γ, in systems of various dimensionalities, may be obtained with the aid of the continuum Green's functions given in Table I. Assuming $\beta \ll D/R^2$, the half-width Γ at half-maximum of the function $\mathrm{Re}[g(\beta+\frac{1}{2}iE)]$, nearly the same as the half-width of $\mathrm{Re}[G(\beta+\frac{1}{2}iE)]$, is given approximately by

$$\Gamma \approx 5.08\beta, \quad \text{1 dimension} \tag{48a}$$

$$\Gamma \approx 2.24[\beta D/R^2]^{1/2}, \quad \text{2 dimensions} \tag{48b}$$

$$\Gamma \approx 1.17 D/R^2, \quad \text{3 dimensions.} \tag{48c}$$

If we regard Γ as an effective dissociation rate of a correlated exciton pair, we see that only in a three-dimensional system is this dissociation rate essentially equal to the exciton hopping rate. In a one-dimensional system this rate is determined primarily by the effective exciton decay rate β, and in a two-dimensional system it depends on the geometric average of the decay and hopping rates.

C. Annihilation Rate, with Spin Relaxation

The calculation of γ becomes considerably more complex when spin relaxation is included, since relaxation causes incoherent transitions among the various spin states which are stationary with respect to the spin Hamiltonian $\mathcal{H}$. The equation of motion for the pair density matrix can then no longer be separated; not even the separation between odd and even spin states can be achieved in general. Approximate expressions for effects of spin relaxation on the annihilation rate are most easily obtained with the aid of the following ansatz for the spin relaxation of the two-exciton density matrix:

$$\left(\frac{\partial}{\partial t}\right)_{\mathbf{rel}}[\rho_2(\mathbf{R})-\tfrac{1}{9}\,\mathrm{Tr}\rho_2(\mathbf{R})\mathbf{1}]$$
$$=-2\zeta[\rho_2(\mathbf{R})-\tfrac{1}{9}\,\mathrm{Tr}\rho_2(\mathbf{R})\mathbf{1}]. \quad (49)$$

According to (49), $\rho_2(\mathbf{R})$ is assumed to relax towards its local equilibrium value, a matrix corresponding to equal occupation of all pair spin states, which should be appropriate to most physical systems at room temperature. The relaxation rate is the same for all matrix elements and is twice the average spin relaxation rate ζ because we are dealing with the relaxation of the spin of two excitons. The ansatz (49) not only assumes a constant relaxation rate but also does not allow the spin of each exciton to relax independently of the other, since *pair* spin states are relaxing towards equilibrium. These deficiencies are remedied in the calculation presented in Appendix C, where a more general relaxation scheme is handled. The complexity of the calculation of Appendix C tends to obscure certain simple features of the effects of relaxation which are contained in the results for the simpler relaxation scheme (49). Moreover, an accurate treatment of the relaxation rates will often not be necessary, e.g, in three-dimensional systems, or in two-dimensional systems where the effective decay rate is comparable to the spin relaxation rate.

To obtain the equation of motion of the density matrix, including spin relaxation via the approximate ansatz, we merely include the right-hand side of (49) in the equation of motion for $\rho_2(\mathbf{R})$, Eq. (30). For the off-diagonal matrix elements of (30), this amounts to replacing β by $\beta+\zeta$; the formal solution for the off-diagonal elements of $\rho_2(\mathbf{R})$ is then the same as (36), but with $\beta+\zeta$ replacing β. To handle the diagonal elements, we first obtain the spin trace of the equation of motion. Since the trace of (49) vanishes, the trace of (30) gives the equation of motion for the spin trace of the pair density matrix, which is just the total probability for the occurrence of two excitons a given distance $\mathbf{R}$ apart. The long-range part of the resulting equation is simple and we immediately obtain the formal result

$$\mathrm{Tr}\rho_2(\mathbf{R})=n^2v^2+g(\mathbf{R},\beta)[\sum_{\mathbf{R}'}\Psi(\mathbf{R}')\,\mathrm{Tr}\rho_2(\mathbf{R}')$$
$$+\beta n^2v^2]+\sum_{\mathbf{R}'}g(\mathbf{R}-\mathbf{R}',\beta)[-\Psi(\mathbf{R}')\,\mathrm{Tr}\rho_2(\mathbf{R}')$$
$$+\tfrac{1}{4}\sum_{l}\langle l|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|l\rangle]. \quad (50)$$

Next, we find the equation of motion of the matrix $\eta(\mathbf{R})\equiv\rho_2(\mathbf{R})-\frac{1}{9}\,\mathrm{Tr}\rho_2(\mathbf{R})\mathbf{1}$; the formal solution for its diagonal elements is, with $V(\mathbf{R})=0$,

$$\langle l|\eta(\mathbf{R})|l\rangle=g(\mathbf{R},\beta+\zeta)[\sum_{\mathbf{R}'}\Psi(\mathbf{R}')\langle l|\eta(\mathbf{R}')|l\rangle]$$
$$+\sum_{\mathbf{R}'}g(R-R',\beta+\zeta)[-\Psi(\mathbf{R}')\langle l|\eta(\mathbf{R}')|l\rangle$$
$$+\tfrac{1}{4}\langle l|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|l\rangle$$
$$-(1/36)\sum_{l'}\langle l'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|l'\rangle]. \quad (51)$$

Equations (50), (51), and the equation for the off-diagonal elements are all readily solved within the smooth approximation; the result can be expressed as a single formula for $\rho_2(\bar{R})$:

$$\langle l|\rho_2(\bar{R})|l'\rangle=\tfrac{1}{4}G[\beta+\zeta+\tfrac{1}{2}i(E_l-E_{l'})]\langle l|M|l'\rangle$$
$$+(\tfrac{1}{3}nv)^2c\delta_{ll'}, \quad (52)$$

where

$$c\equiv 1+\tfrac{1}{4}(nv)^{-2}[G(\beta)-G(\beta+\zeta)]\sum_{l''}\langle l''|M|l''\rangle \quad (53)$$

and

$$M\equiv\Lambda\rho_2(\bar{R})+\rho_2(\bar{R})\Lambda. \quad (54)$$

The function G has been defined in (38). Equation (52) is solved as when spin relaxation was absent, treating c as a constant. The quantity c is then determined self-consistently. Λ is assumed to have the form $\Lambda=\lambda_SP_S+\lambda_TP_T$, where P_S and P_T are, respectively, projection operators into the singlet and the triplet manifolds of pair states. It is clear from the form of (52) that the resulting expressions for the annihilation rates γ_T and γ_S are just c times those given in (32) and (42), with the quantities A_l of the latter formula being determined by (43), provided the decay rate β is everywhere replaced by $\beta+\zeta$. The quantity c is most easily expressed with the aid of the fact that in its definition, Eq. (53), the total singlet- and triplet-channel annihilation rates appear directly. These may in turn be expressed in terms of the rate constants γ_S and γ_T, and we find

$$c=1+\tfrac{1}{2}[G(\beta)-G(\beta+\zeta)][2\gamma_T/v+\gamma_S/v] \quad (55a)$$

or, since c is implicitly contained in γ_T and γ_S, in the form $\gamma_T=c\gamma_T{}^0$, $\gamma_S=c\gamma_S{}^0$, we have

$$c^{-1}=1-\tfrac{1}{2}[G(\beta)-G(\beta+\zeta)][2\gamma_T{}^0/v+\gamma_S{}^0/v], \quad (55b)$$

where now $\gamma_T{}^0$ and $\gamma_S{}^0$ may be calculated from formulas previously given.

It is seen that the main effects of spin relaxation are an increase of the effective decay rate and an over-all reduction in the annihilation rates via c [c is less than 1, since $G(\beta)<G(\beta+\zeta)<0$]. The magnetic field dependence of c, via $\gamma_S{}^0$, leads to some magnetic field dependence of the triplet-channel annihilation and causes some smoothing out of the magnetic field effects in the singlet-channel annihilation rate. These latter effects will be weak if either γ_T^0 is large compared to γ_S^0 or if $1-c$ is small.

V. TRIPLET EXCITONS IN ANTHRACENE

In this section, we relate our theory of exciton-exciton annihilation to experimental observations on triplet excitons in anthracene at room temperature. The various approximations of the theory are checked quantitatively and predictions of the theory are compared with available data.

A. Exciton Motion

Both theoretical considerations[15,16] and recent experimental findings[22] point to triplet exciton motion in anthracene as being essentially two-dimensional, with diffusion confined mainly to the *ab* plane and only weak diffusion perpendicular to this plane. This circumstance is of crucial importance in the theory of exciton annihilation, as we have seen. The microscopic motion at room temperature can be characterized in terms of a hopping model,[24] with allowed hops occurring between certain nearest neighbors only. We shall assume that the only nonzero hopping rates are

$$\begin{aligned}&\Psi[\tfrac{1}{2}(\mathbf{a}\pm\mathbf{b})]=\Psi[-\tfrac{1}{2}(\mathbf{a}\pm\mathbf{b})]\equiv\Psi_d\,,\\&\Psi(\pm\mathbf{b})\equiv\Psi_b\,,\\&\Psi[\pm\mathbf{c}\mp\tfrac{1}{2}(\mathbf{a}+\mathbf{b})]\equiv\Psi_{c^*}\,,\end{aligned}$$

where **a**, **b**, **c** are the lattice vectors of the anthracene crystal. We also assume $\Psi_d=2\Psi_b$, a relation which yields isotropic diffusion in the *ab* plane and is consistent with the experimental observations.[22] The quantity Ψ_{c^*}, even though it is small compared to Ψ_d and could even be comparable to $\Psi(\mathbf{a})$, which has been neglected, has been retained as characterizing out-of-plane motion. We have seen that such out-of-plane motion, though slow, contributes to the effective lifetime of an annihilating pair in a two-dimensional system.

The values of the hopping parameters can be deduced from the measured values of the diffusion tensor and the lattice constants, via Eq. (23). Using Ern's[22] measurements of the diffusion tensor, and the lattice structure of anthracene,[28] we have

$$\begin{aligned}\Psi_d=2D_{aa}/a^2=2(1.5\times10^{-4}\text{ cm}^2\text{ sec}^{-1})/&\\(8.56\times10^{-8}\text{ cm})^2=4.1\times10^{10}\text{ sec}^{-1}\,,&\\\Psi_{c^*}\equiv D_{c^*c^*}/(c^*)^2=1.2\times10^{-5}\text{ cm}^2\text{ sec}^{-1}/&\\(9.16\times10^{-8}\text{ cm})^2=1.4\times10^{9}\text{ sec}^{-1}\,,&\end{aligned}$$

where $\mathbf{c}^*$ is the vector parallel to $\mathbf{a}\times\mathbf{b}$, with magnitude equal to the projection of **c** along this direction, i.e., c^* is the distance between *ab* planes. For experimental reasons, it is possible that the true Ψ_{c^*} is considerably smaller than the value given. In any event, the intrinsic exciton decay rate $\beta\approx50$ sec^{-1} is negligible compared to Ψ_{c^*}, which therefore is just the effective decay rate β_{eff} [Eq. (27)] for this nearly two-dimensional system, if spin relaxation can be neglected.

The Green's function $g(\mathbf{R},\beta)$ will for $R\neq0$ be approximated by

$$g(\mathbf{R},\beta)=-(v_{ab}/2\pi D)K_0[(\beta/D)^{1/2}R]\,,\tag{56}$$

where $D=D_{aa}$ and v_{ab} is the area per molecule in the *ab* plane, $v_{ab}=25.8\times10^{-16}$ cm^2. For $\beta=1.4\times10^9$ sec^{-1}, the quantities $g(\mathbf{b},\beta)$ and $g[\frac{1}{2}(\mathbf{a}+\mathbf{b}),\beta]$ differ by about 8%. The smooth approximation, where R will be replaced by the average length of the six lattice vectors $\pm b$, $\pm\frac{1}{2}(\mathbf{a}\pm\mathbf{b})$, $\bar{R}=5.5\times10^{-8}$ cm, should not lead to errors of more than 5%, although the error may increase when spin relaxation is added. The smooth approximation is also used to obtain $g(0,\beta)$, needed in Eq. (38), by relating it to $g(\bar{R},\beta)$ with the aid of Eq. (20).

B. Spin Hamiltonian

As is well known, the spin Hamiltonian for a triplet state of the anthracene molecule can be well approximated by the expression

$$\mathcal{H}=D(S_z^2-\tfrac{1}{3}S^2)+E(S_x^2-S_y^2)\,,\tag{57}$$

where **S** is the spin operator for triplets, and where the principal axes *x*, *y*, *z* are, respectively, the long, medium, and normal axes of the anthracene molecule. For excitons in the crystal, which contains two different orientations of anthracene molecules,[28] the Hamiltonian is the average of (57) over the two orientations.[26,29] This average can also be cast into the form (57), and the full single-exciton Hamiltonian, including an external magnetic field **H**, has the form

$$\mathcal{H}=g\mu_B\mathbf{H}\cdot\mathbf{S}+D^*(S_{z^*}^2-\tfrac{1}{3}S^2)+E^*(S_{x^*}^2-S_{y^*}^2)\,.\tag{58}$$

Values of the parameters D, E, D^*, E^* have been determined from spin-resonance experiments.[29] For purposes of comparing the theory with the magnetic field experiments on exciton-exciton annihilation, it is convenient to adopt units such that $g\mu_B=1$. With $g=2.0$,[29] the zero-field parameters given in Ref. 29 are then

$$D=737\text{ Oe}\,,\qquad E=-87\text{ Oe}\,,$$
$$D^*=-62\text{ Oe}\,,\qquad E^*=350\text{ Oe}\,.$$

The z^* axis is along **b**, while x^* lies in the *ac* plane, at an angle of 27.4 deg from the *a* axis.[29]

C. Spin Relaxation

The dominant mechanism of spin relaxation of triplet excitons in anthracene is expected to arise from the random motion of the excitons between the two differently oriented molecules of the crystal.[26] Since the

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[28] A. McL. Mathieson, J. M. Robertson, and V. C. Sinclair, Acta Cryst. **3**, 245 (1950); **3**, 251 (1950).

[29] D. Haarer, D. Schmid, and H. C. Wolf, Phys. Status Solidi **23**, 633 (1967).

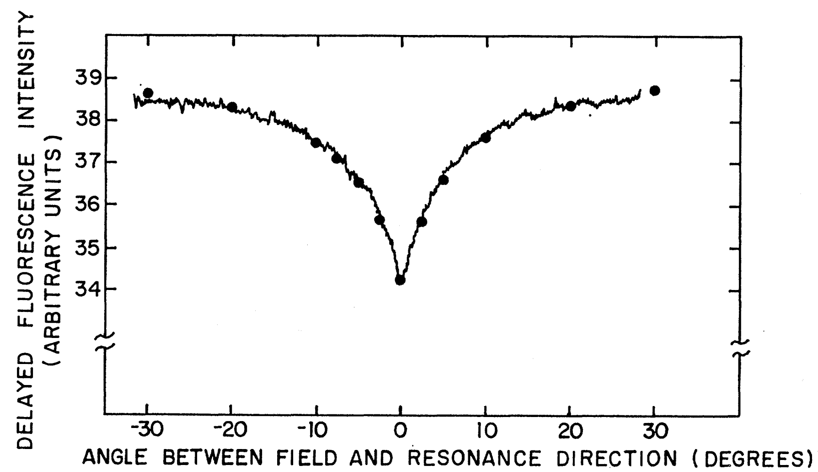

FIG. 1. Comparison of experimental and theoretical resonance shape. The wiggly curve is a reproduction of the high-field resonance shape observed by Johnson (Ref. 23), for delayed fluorescence from anthracene in the presence of a magnetic field of 4000 Oe, oriented parallel to the *ac* plane of anthracene. Points are theoretical results, for values of the parameters stated in the text.

orientations of these molecules, their spin Hamiltonians, as well as the exciton hopping rates at room temperature are all known quantities, it is possible to obtain an accurate evaluation of the spin relaxation rate. Recent theories of this relaxation rate[30] do not treat the exciton motion accurately. A more complete theory of spin relaxation via exciton hopping is presented in Appendix D. For purposes of comparing the present theory with the magnetic field experiments on delayed fluorescence, it turns out that the knowledge of an average relaxation rate ζ is sufficient. As shown in Appendix D, for magnetic fields small compared to about 20 kOe this rate is independent of the field and is given by an expression of the form

$$\zeta=(E')^2/6\Psi_d, \tag{59}$$

where E' depends on the spin Hamiltonian and molecular orientations and has for anthracene the value 255 Oe. Using $\Psi_d=4.1\times10^{10}$ sec^{-1}, the value of ζ is 8.2×10^7 sec^{-1}, or $\hbar\zeta/g\mu_B=4.65$ Oe. Although this value is an order of magnitude less than the hopping rate Ψ_{c^*} implied by Ern's measurements, we must not conclude that spin relaxation gives a negligible contribution to the effective pair decay rate. As pointed out by Ern,[22] the measured value of $D_{c^*c^*}$, and hence of Ψ_{c^*}, is only an upper limit to the intrinsic value, since crystal imperfections tend to increase the measured value. It is possible to resolve this question experimentally by studying delayed fluorescence in the presence of high magnetic fields. At fields in excess of about 20 kOe, the spin relaxation rate becomes small and any observed changes in the effective decay rate at such fields would attest to the relative importance of spin relaxation and out-of-plane diffusion.

D. Comparison with Experiment

Granting the validity of various approximations made in the present theory, there remain essentially three unknown parameters in the description of triplet exciton annihilation in anthracene at room temperature: the total *ab*-plane nearest-neighbor annihilation-rate constants in the singlet and triplet channels, λ_S and λ_T, and the out-of-plane hopping rate Ψ_{c^*}, for which we at least have an upper limit.

We now present an approximate fit of the present theory to the observed magnetic field dependence of delayed fluorescence from anthracene crystals at room temperature.[23] In this fit the parameters λ_S and Ψ_{c^*} are treated as adjustable; the parameter λ_T can be neglected provided it is of the same order of magnitude as λ_S. We ignore differences between the various spin relaxation rates, using a single average rate ζ. We also neglect deviations from unity of the coefficient c, Eq. (53) or (55), an assumption that will be justified after the values of the various parameters have been determined. The theory then becomes the same as for the case of negligible spin relaxation, the decay rate β being replaced by $\Psi_{c^*}+\zeta$. In fitting to experiment, we solve Eq. (43) numerically for variable values of β and λ_S, using the approximation (56) and the value $D=1.5\times10^{-4}$ cm^2 sec^{-1} for the diffusion constant.

We find that it is not possible to achieve a perfect fit to all available data for any choice of β and λ_S. A reasonable fit can, however, be obtained for a fairly wide range of these parameters. The fit judged as best is illustrated in Figs. 1–3, for what is believed to be a representative sampling of the observed dependence of delayed fluorescence from anthracene on both the direction and magnitude of the applied magnetic field. Of these, Fig. 1 shows a particularly careful experimental determination of the resonance line shape, a quantity that is of central importance in the present theory. A very good fit to this resonance shape has been found. The values of the parameters for which the fit is shown are $\beta/2\mu_B=16$ Oe and $k=1.0$, where the parameter k is related to λ_S via (43). The quality of the fit is not too sensitive to changes in β and λ_S, and values of these parameters in the ranges 5 Oe$<\beta/2\mu_B<$25 Oe, $0.8<k$

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[30] H. C. Wolf (private communication); Z. G. Soos, J. Chem. Phys. **51**, 2107 (1969).

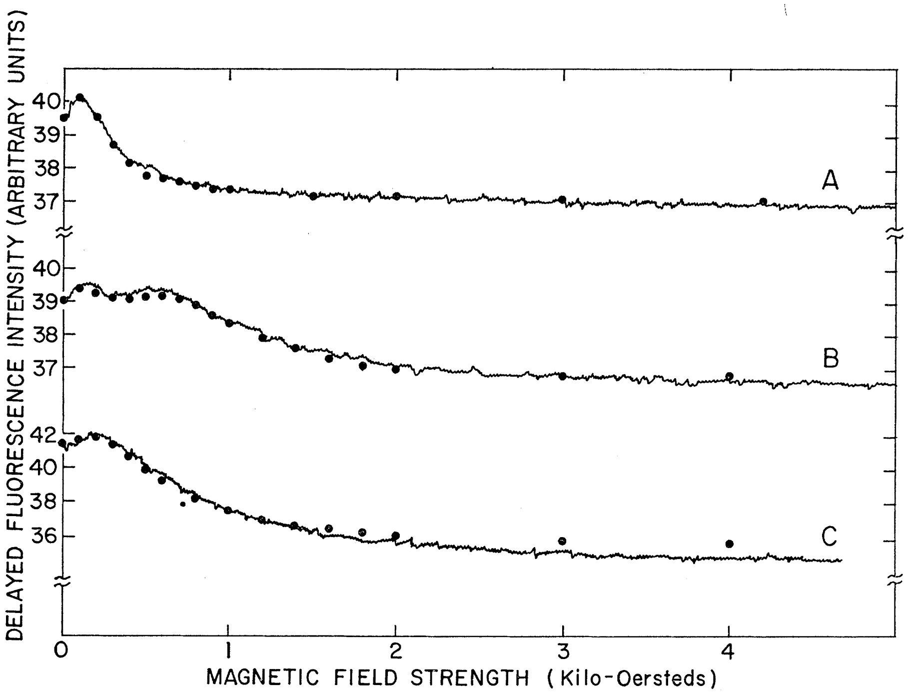

FIG. 2. Comparison of experimental and theoretical magnetic field strength dependence of delayed fluorescence. Johnson's (Ref. 23) observations (wiggly curves) on anthracene are compared with the present theory (points) for the following orientations of the magnetic field: curve A, **H** along the x^* axis of the zero-field Hamiltonian; curve B, **H** in the *ac* plane, forming an angle of 20° with the x^* axis; curve C, **H** along the *b* crystal axis.

<1.2 cannot be ruled out. We have attempted to improve the fit by performing the calculation for several other values of the diffusion constant D, but found that no significant improvement could be achieved. We have also made calculations in which variations in the spin relaxation rate, according to the theory given in Appendices C and D, were explicitly included. The results differ from those of the constant-relaxation-rate theory only when $\beta/2\mu_B$ is close to 5 Oe, when out-of-plane diffusion effects are relatively unimportant (since $\zeta/2\mu_B=4.65$ Oe); a fit as good as the one shown could not be obtained in this limit. The slight disagreement between theory and experiment may thus be attributable to errors due to approximations made in the theory. The parameters determined in the fit in effect determine the total nearest-

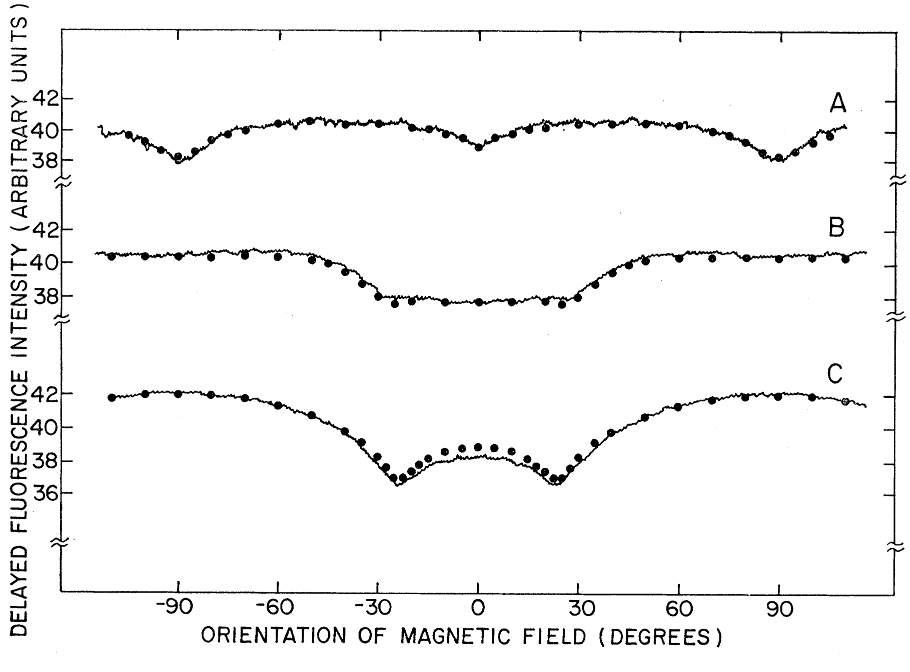

FIG. 3. Comparison of experimental and theoretical dependences of delayed fluorescence on the orientation of magnetic field. Johnson's (Ref. 23) observations (wiggly curves) on anthracene are compared with the present theory (points) for magnetic fields as follows. Curve A: $H=400$ Oe, field in *ac* plane; curve B: $H=600$ Oe, field in *ab* plane; curve C: $H=4000$ Oe, field in *ab* plane. For curves B and C, the angle is chosen to be zero along the *b* axis; for curve A, the zero angle is taken along the y^* axis of the zero-field Hamiltonian.

neighbor singlet-channel annihilation rate λ_S and the out-of-plane component of the diffusion tensor $D_{c^*c^*}$. We find

$$\lambda_S=(3\pm0.5)\times10^{11}\ \text{sec}^{-1},$$

$$\Psi_{c^*}=\beta-\zeta=(2\pm1)\times10^{8}\ \text{sec}^{-1},$$

$$D_{c^*c^*}=(1.7\pm0.8)\times10^{-6}\ \text{cm}^2\ \text{sec}^{-1}.$$

With these values, the error introduced by approximating the quantity c by unity is less than about

$$\lambda_S[G(\beta+\zeta)-G(\beta)]/[18(1+k)]\approx0.5\%. \qquad (60)$$

If the triplet-channel annihilation rate is large compared to the singlet-channel rate, the error introduced in the relative variations in γ_S will be further decreased; since only such relative variations were used in obtaining the fit to experiment, the corrections due to $c\neq1$ can indeed be ignored. The actual value of γ_S will, however, be in error in this case [see Eq. (55)]. If this error is neglected, the predicted zero-field value of the annihilation rate constant γ_S is calculated to be

$$\gamma_S=(\tfrac{1}{9}v\lambda_S)\times(0.62\pm0.04)$$
$$=(5\pm1)\times10^{-12}\ \text{cm}^3\ \text{sec}^{-1}.$$

This value will be reduced if γ_T is large compared to γ_S; with the aid of (55) and (60), the error introduced by neglecting γ_T becomes comparable to the uncertainty in the above value only when $\gamma_T/\gamma_S\gtrsim20$. There is no direct measurement of γ_S available for comparison. The rate constant usually measured is[14] $f^{-1}\gamma_{\text{tot}}$, where f is the fraction of triplet-triplet annihilations which lead to delayed fluorescence, and $\gamma_{\text{tot}}=\gamma_S+\gamma_T$. The value for $f^{-1}\gamma_{\text{tot}}$ is about[14] 5×10^{-11} cm^3 sec^{-1}, with an error of at least 50%. If we assume that all singlet-channel annihilations lead to delayed fluorescence, then the experimental value of γ_S is about $f^2\times5\times10^{-11}$ cm^3 sec^{-1}. Recent measurements,[31] as well as the estimate of Helfrich and Schneider,[32] but the value of f at around 0.4, giving a value of $(8\pm4)\times10^{-12}$ cm^3 sec^{-1} for the value of γ_S, in agreement with the quasiexperimental value we have found. This value of f also justifies the neglect of γ_T in the calculation of γ_S.

VI. DISCUSSION

We have endeavored to present a fairly general picture of the kinematics of exciton-exciton annihilation, although we have leaned towards features characteristic of triplet excitons in anthracene. In particular, we have tried to emphasize the importance of the fact that two-dimensional exciton motion leads to qualitatively different results from those of the three-dimensional theory used heretofore. If triplet-exciton motion in anthracene were three-dimensional, with the same diffusion constant and spin Hamiltonian, most of the magnetic field effects on the annihilation rate would become essentially unobservable, because of the great broadening of the shape function [see Eq. (48)]. The observation of these effects therefore provides strong evidence for the nearly two-dimensional nature of triplet excitons in anthracene, in support of theory[15,16] and of Ern's[22] observations, but in disagreement with reported nearly isotropic diffusion.[33]

The theory should also improve our insight into the physical origin of the magnetic field effects. These effects arise because excitons can collide repeatedly, while their spin wave functions evolve as a function of time between each collision. We have shown that the detailed time dependence of the collision and recollision process is contained in the shapes of the directional resonances and have developed a quantitative theory of such shapes, thus placing this intuitive picture on a somewhat firmer basis. The importance of repeated collisions also accounts for the requirement that a system be one- or two-dimensional if magnetic field effects are to be significant: In a three-dimensional system, as we have seen in the Introduction, the probability of recollision is rather small.

It is perhaps worthwhile to attempt an interpretation of the crude, but much simpler kinetic scheme (4) for describing exciton annihilation, used in previous treatments.[15,16,18,23] In terms of the present theory, this scheme can be understood as follows: Suppose we consider a pair of excitons as being in the compound state (TT) whenever they are less than some distance R_c apart, and consider them isolated when their separation exceeds R_c. Let us at first turn off exciton-exciton annihilation; at equilibrium, the density of compound pairs is then given by $(k_1/k_{-1})n^2$, where n is the exciton density. But in the absence of annihilation this density must equal the density of random coincidences of two excitons happening to be less than R_c apart, which is just n^2V, where V is the volume (respectively area or length) of the region $r<R_c$. Therefore, $k_1/k_{-1}=V$. Insofar as we may estimate k_{-1} by means of the expressions (48) for the half-widths Γ, we may obtain an idea of the size of the volume V in various dimensions, using for k_1 the expressions for γ_∞ given in Table I. The results, omitting factors of the order of unity, are as follows:

$$V\sim vL/R, \qquad \text{1 dimension}$$

$$V\sim v\frac{(L/R)}{\ln(L/R)}, \qquad \text{2 dimensions}$$

$$V\sim v, \qquad \text{3 dimensions}$$

where v is the volume per molecule of the crystal, L is the healing length $(D/\beta)^{1/2}$, with β the total effective

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[31] J. Fourny and G. Delacote (unpublished); R. P. Groff, R. E. Merrifield, and P. Avakian, Chem. Phys. Letters (to be published).

[32] W. Helfrich and W. G. Schneider, J. Chem. Phys. **44**, 2902 (1966).

[33] M. Levine, J. Jortner, and A. Szoke, J. Chem. Phys. **45**, 1591 (1966); G. Durocher and D. F. Williams, *ibid.* **51**, 1675 (1969).

decay rate (including spin relaxation for triplets), and R is an average lattice spacing. It has been assumed that $R \gg L$. We see that only in three dimensions is it legitimate to think of the state (TT) as consisting of a nearest-neighbor pair. In one dimension, excitons must be considered as correlated in this model whenever they are less than a healing length apart, i.e., whenever the exciton pair distribution function differs appreciably from its uncorrelated value. As usual, the two-dimensional case lies somewhere between these two extremes. The annihilation rate constant k_2 represents the average annihilation rate of all pairs whose separation is less than R_c; since only nearest-neighbor pairs actually annihilate (let us so assume), this average rate is roughly $k_2 \sim \lambda v/V$.

The quantitative agreement of theory and experiment, for triplets in anthracene, seems to be satisfactory, but not perfect. The exact source of the slight disagreements is not certain, and could be a combination of the simplifying assumptions of the theory and possible systematic experimental errors. A perhaps more severe source of error, and one that could not be dismissed easily, would be present if there exists an exciton-exciton interaction which is comparable, in appropriate units, to the nearest-neighbor annihilation rate. Such an interaction could conceivably arise via induced lattice distortions and, be it attractive or repulsive, could influence the detailed kinematics of the collision process.

It should be emphasized that the present theory is applicable only at large temperatures, such that excitons satisfy a hopping equation of motion and have uniformly populated spin states. Both of these conditions are expected to be violated at low temperatures. Although it is relatively simple to modify the present theory so as to include a nonrandom distribution of spin states, the inclusion of band effects would necessitate a new theory, since the exciton pair density matrix can no longer be assumed to be spatially diagonal when coherent intramolecular exciton motion occurs.

ACKNOWLEDGMENTS

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APPENDIX A: EQUATION FOR CONTINUUM CORRELATION FUNCTION

We describe the exciton system by a set of distribution functions $f_N(N;\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$, giving the probability that there are N excitons in the system times the probability density for these excitons being at $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N$. From these, the average j-particle distribution functions are obtained as

$$f_j(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_j) \equiv \sum_{N=j}^{\infty} (N-j)!^{-1} \int d\mathbf{r}_{j+1} \int d\mathbf{r}_{j+2} \cdots \times \int d\mathbf{r}_N\, f_N(N;\mathbf{r}_1,\ldots,\mathbf{r}_N). \tag{A1}$$

For a noninteracting system, and one in which the particle number is random with expectation value N_0, these distribution functions become

$$f_j(\mathbf{r}_1,\ldots,\mathbf{r}_j)_{\text{nonint}} = n^j, \tag{A2}$$

where $n = N_0/V$ is the particle density, with V the total volume of the system.

The equations of motion are clear-cut for the functions $f_N(N_j\cdots)$. Suppressing the implicit time variable, we have

$$\frac{\partial}{\partial t} f_N(N;\mathbf{r}_1,\ldots,\mathbf{r}_N) = D \sum_{i=1}^{N} \nabla_i^2 f_N(N;\mathbf{r}_1,\ldots,\mathbf{r}_N) - N\beta f_N(N;\mathbf{r}_1,\ldots,\mathbf{r}_N) + \beta \int d\mathbf{r}\, f_{N+1}(N+1;\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{r})$$
$$+\alpha \sum_{i=1}^{N} f_{N-1}(N-1;\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N) - \alpha V f_N(N;\mathbf{r}_1,\ldots,\mathbf{r}_N) - \sum_{i<j} \lambda(r_i - r_j) f_N(N;\mathbf{r}_1,\ldots,\mathbf{r}_N)$$
$$+\tfrac{1}{2} \int d\mathbf{r} \int d\mathbf{r}'\, \lambda(\mathbf{r}-\mathbf{r}') f_{N+2}(N+2;\mathbf{r}_1,\ldots,r_N,r,r'). \tag{A3}$$

In writing the above equation, we simply have to keep in mind conservation of probability—e.g., a two-exciton decay process transfers probability from $(N+2)$-exciton states to N-exciton states, for *all* N.

The equations of motion for the one- and two-particle distribution functions are obtained from (A3) by straightforward integrations and summations. To avoid spurious boundary terms, it is convenient to assume that all particles move in a large region with periodic boundary conditions. The equations for f_2 and f_1 are

$$\frac{\partial}{\partial t} f_2(\mathbf{r}_1,\mathbf{r}_2) = D(\nabla_1^2 + \nabla_2^2) f_2(\mathbf{r}_1,\mathbf{r}_2)$$
$$-2\beta f_2(\mathbf{r}_1,\mathbf{r}_2) + \alpha[f_1(\mathbf{r}_1) + f_2(\mathbf{r}_2)]$$
$$-\lambda(\mathbf{r}_1-\mathbf{r}_2) f_2(\mathbf{r}_1,\mathbf{r}_2) - \int d\mathbf{r}_3 [\lambda(\mathbf{r}_1-\mathbf{r}_3)$$
$$+\lambda(\mathbf{r}_2-\mathbf{r}_3)] f_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \tag{A4}$$

and

$$\frac{\partial}{\partial t}f_1(\mathbf{r}_1)=D\nabla_1^2 f_1(\mathbf{r}_1)-\beta f_1(\mathbf{r}_1)+\alpha - \int d\mathbf{r}_2\, \lambda(\mathbf{r}_1-\mathbf{r}_2) f_2(\mathbf{r}_1,\mathbf{r}_2). \quad \text{(A5)}$$

Equations (6) and (7) result from these when $f_1(\mathbf{r}_1)$ is equal to the uniform density $n(t)$, and with $f(\mathbf{r},t) = f_2(\mathbf{r}_0+\mathbf{r},\ \mathbf{r}_0)$, $g(\mathbf{r},\mathbf{r}',t) = f_3(\mathbf{r}_0+\mathbf{r},\ \mathbf{r}_0+\mathbf{r}',\ \mathbf{r}_0)$, for arbitrary $\mathbf{r}_0$.

APPENDIX B: QUANTUM-MECHANICAL DESCRIPTION OF ANNIHILATION

The aim here will be to derive equations analogous to those of Appendix A but taking into account both the quantum-mechanical nature of the excitons and the discreteness of the lattice in which they move. Since a quantum-mechanical description of the spatial motion has been given elsewhere[24] and since the treatment of the spin time development is elementary, we concentrate on the derivation of the general form of exciton nonconserving parts of the equation of motion of the exciton density matrix, particularly the term describing exciton annihilation.

We introduce the exciton annihilation and creation operators $a_n(\mathbf{R})$ and $a_n^\dagger(\mathbf{R})$ which, respectively, annihilate and create an exciton on the lattice point $\mathbf{R}$ in a spin state $|n\rangle$. These operators satisfy the relations

$$\begin{aligned} &[a_n(\mathbf{R}),a_m^\dagger(\mathbf{R}')]_- = [a_n(\mathbf{R}),a_m(\mathbf{R}')]_- = 0 \\ &\qquad\qquad\qquad\qquad \text{when} \quad \mathbf{R}\neq\mathbf{R}', \\ &[a_n(\mathbf{R}),a_n^\dagger(\mathbf{R})]_+ = 1, \\ &a_n(\mathbf{R})a_m(\mathbf{R}) = a_n(\mathbf{R})a_m^\dagger(\mathbf{R}) = 0, \end{aligned} \quad \text{(B1)}$$

where excitons have been constrained such that two excitons cannot occupy the same lattice site, regardless of spin.

Let ρ be the complete density matrix of the many-exciton system, including nonexcitonic degrees of freedom such as lattice vibrations. This density matrix is the equivalent of the classical set of distribution functions f_N. The j-exciton density matrix ρ_j is a partial trace of ρ, such that j excitons are fixed in definite states; it is analogous to (A1). The creation and annihilation operators just introduced help us express ρ_j in the form

$$\begin{aligned} \langle n_1,n_2,\ldots,n_j|\,\rho_j(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_j)\,|m_1,m_2,\ldots,m_j\rangle &= \mathrm{Tr}[\rho a_{n_1}^\dagger(\mathbf{R}_1)a_{n_2}^\dagger(\mathbf{R}_2)\cdots a_{n_j}^\dagger(\mathbf{R}_j)a_{m_1} \\ &\quad \times(\mathbf{R}_1)a_{m_2}(\mathbf{R}_2)\cdots a_{m_j}(\mathbf{R}_j)], \end{aligned} \quad \text{(B2)}$$

where we have defined only the spatially diagonal part of ρ_j, the only part with which we need to concern ourselves within the hopping model.

Suppose now the system Hamiltonian contains small exciton nonconserving terms. We wish to describe the time development of ρ, treating these terms as a perturbation. The difficulty in doing this is that the changes in ρ introduced by such terms cannot be kept arbitrarily small, since they grow in time. A way to handle such a problem has been described by Lax.[34] The presence of exciton-nonconserving terms in the Hamiltonian leads to matrix elements of ρ between states of different exciton number; these matrix elements can be made arbitrarily small compared to the exciton-conserving matrix elements and thus serve as a basis for perturbation. Adapting Lax's technique to the present problem, we write $\rho=\rho_c+\delta\rho$, where ρ_c is the exciton-conserving part. The Hamiltonian is written as $\mathcal{H}+V$, where V is the small nonconserving interaction. To lowest order in the nonconserving terms, the equations for ρ_c and $\delta\rho$ then have the form

$$i\frac{\partial}{\partial t}\rho_c = [\mathcal{H},\rho_c]+[V,\delta\rho], \quad \text{(B3)}$$

$$i\frac{\partial}{\partial t}\delta\rho = [\mathcal{H},\delta\rho]+[V,\rho_c]. \quad \text{(B4)}$$

Equation (B4) may be integrated for $\delta\rho$ in terms of ρ_c if we switch V off adiabatically as $t\rightarrow-\infty$, i.e., replace V by Ve^{0^+t}. If the result is substituted in (B3), one obtains

$$i\frac{\partial}{\partial t}\rho_c(t) = [\mathcal{H},\rho_c(t)] + \left(V, i\int_0^\infty dt' e^{-0^+t'} e^{-i\mathcal{H}t'}[V,\ \rho_c(t-t')]e^{i\mathcal{H}t'}\right). \quad \text{(B5)}$$

The crucial step in simplifying (B5) consists in arguing that the integrand in (B5) will be important only for small t', such that $\exp(-i\mathcal{H}t')\rho(t-t')\exp(i\mathcal{H}t') \approx \rho_c(t)$. To make this argument we must first of all keep in mind the fact that (B5) will always be used in conjunction with a trace. We will be interested in quantities of the form $\mathrm{Tr}[\rho M]$, where M is an exciton operator and conserves exciton number. Thus M will not have significant matrix elements between states having the same exciton occupations but differing greatly in their nonexcitonic parts. As a consequence, the important matrix elements of ρ in the trace will be those between states having nearly the same nonexcitonic configurations. Such matrix elements arise in Eq. (B5) only from small t', since the operator $\exp(-i\mathcal{H}t')V\exp(i\mathcal{H}t')$ describes the time evolution of the state produced upon creation or annihilation of appropriate excitons. This state, after times of the order of an exciton scattering time ($\sim 10^{-14}$ sec in anthracene[24]), will bear little resemblance to the initial state. In other words, the approximation of neglecting contributions to (B5) from times t' comparable to and

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[34] M. Lax, Phys. Rev. **145**, 110 (1966).

greater than the decay time determined by V will be valid whenever the lattice scattering time is short compared to this decay time.

A further simplification can be made if we write the interaction V in the general form

$$V=\sum_j A_jB_j^\dagger+A_j^\dagger B_j\,, \tag{B6}$$

where A_j are exciton operators which destroy excitons while B_j refer only to nonexcitonic degrees of freedom. The simplification consists in approximating the time development of V, for small times, by

$$V(t)=\sum_j A_jB_j^\dagger(t')\exp(-iE_jt') +A_j^\dagger B_j(t')\exp(iE_jt')\,, \tag{B7}$$

where we have abbreviated $V(t')\equiv\exp(-i\mathcal{H}t')V\exp(i\mathcal{H}t')$, and where E_j is an average energy of the excitons destroyed by A_j. For spinless excitons whose motion can be described in the hopping model, the approximation (B7) will be applicable provided A_j destroys excitons in localized states, since the latter are nearly stationary and vary slowly compared to the exciton scattering rate, a rate characteristic of the changes in the nonexcitonic variables. When spin is included we also require that the latter rate be large compared to the rate of spin motion, or, equivalently, that the spin Hamiltonian be small compared to the Hamiltonian describing motion of the nonexcitonic degrees of freedom. We expect this relation to hold even in the presence of large magnetic fields, e.g., in anthracene, where the exciton scattering time is less than 10^{-13} sec at room temperature, fields of the order of 5×10^5 G would be needed to make the spin motion as rapid as the scattering.

In describing exciton decay and production processes, we will need the equation of motion for the expectation value $\langle M\rangle=\mathrm{Tr}(\rho M)$ of certain exciton-conserving exciton operators M. We will be interested in this equation of motion only on a time scale characteristic of the exciton spatial and spin motion and of changes in the exciton population. As we have pointed out, this time scale will be large compared to the time scale in which changes in the nonexcitonic variables take place. Accordingly, we may average over the latter degrees of freedom. Before performing this average, we observe that only exciton-conserving terms survive the trace involved in the equation of motion for $\langle M\rangle$. That means that in Eq. (B5), upon substitution of (B7), we need keep only those terms which involve the exciton-conserving combinations $A_j^\dagger A_k$ or $A_jA_k^\dagger$. If we now perform the average, over the nonexcitonic variables, of the exciton-conserving part of (B5), we encounter averages of the form $\langle B_jB_k^\dagger(t')\rangle$ and $\langle B_j^\dagger B_k(t')\rangle$, as well as their complex conjugates. The second of these vanishes if we are dealing with exciton-destroying processes, for B_k destroys states which result immediately upon an exciton annihilation event described by A_k. Such states must be nonequilibrium states if exciton destruction is to take place. Similarly, $\langle B_jB_k^\dagger(t')\rangle$ vanishes for production processes.

The equation describing destruction processes then takes the form

$$\frac{\partial}{\partial t}\langle M\rangle=-i\langle[M,\mathcal{H}]\rangle-\sum_{j,k}\langle\mu_{jk}MA_j^\dagger A_k +\mu_{jk}^*A_k^\dagger A_jM-\mu_{jk}A_j^\dagger MA_k-\mu_{jk}^*A_k^\dagger MA_j\rangle\,, \tag{B8}$$

where μ_{jk} is the complex quantity

$$\mu_{jk}=\int_0^\infty dt'\,e^{-0^+t'-iE_kt'}\langle B_jB_k^\dagger(t')\rangle\,. \tag{B9}$$

For production processes, the roles of A and $A^\dagger$ and of B and $B^\dagger$ are interchanged in the above. In all the cases we shall consider, it will be possible to make a choice of the combinations of operators A_j, B_j such that (B9) vanishes when $j\neq k$. If for $j\neq k$, A_j and A_k destroy localized excitons on different sets of lattice sites, for example, then the corresponding operators $B_j^\dagger$ and $B_k^\dagger$ also produce differently located localized states. Insofar as these states have neligible overlap, (B9) will then be negligible. If A_j and A_k destroy excitons on the same set of lattice sites, but with different spin quantum numbers, (B9) will vanish for $j\neq k$ if these spin quantum numbers are conserved in the annihilation process.

When (B9) is nonzero only if $j=k$, it is easy to see from (B8) that the imaginary part of μ_{jj} gives a correction to the total Hamiltonian, and so is of no further interest. The decay is governed by the real part of μ_{jj}, which may be rewritten in the form of Fermi's golden rule

$$\begin{aligned}\mathrm{Re}\mu_{jj}&=\mathrm{Re}\int_0^\infty dt\,e^{-0^+t}\times\sum_{s,s'}\langle s|\rho B_j|s'\rangle\langle s'|B_j|s\rangle e^{-i(E_s-E_{s'}+E_j)t}\\&=\sum_{s,s'}W_s|\langle s|B_j|s'\rangle|^2\pi\delta(E_s-E_{s'}+E_j)\,,\end{aligned} \tag{B10}$$

where $|s\rangle$ are stationary states of the unperturbed Hamiltonian, having energies E_s and statistical weight factors W_s.

We now apply (B8) to specific cases.

(*a*) *Monomolecular exciton decay.* We can readily calculate the equation for the general j-exciton density matrix, choosing

$$M=a_{n_1}^\dagger(\mathbf{R}_1)\cdots a_{n_j}^\dagger(\mathbf{R}_j)a_{m_1}(\mathbf{R}_1)\cdots a_{m_j}(\mathbf{R}_j)\,.$$

The operators A_j are given by $a_n(\mathbf{R})$ in this case, and μ_{jj} is independent of j if the decay is to be spin independent and spatially uniform. We obtain, with the aid of the relations (B1),

$$\left(\frac{\partial}{\partial t}\right)_{\text{decay}} \langle n_1,\ldots,n_j|\rho_j(\mathbf{R}_1,\ldots,\mathbf{R}_j)|m_1,\ldots,m_j\rangle$$
$$= -j\beta\langle n_1,\ldots,n_j|\rho_j(\mathbf{R}_1,\ldots,\mathbf{R}_j)|m_1,\ldots,m_j\rangle, \quad \text{(B11)}$$

where $\beta = 2\,\mathrm{Re}\mu$, and where only the decay part of the time derivative has been displayed.

(*b*) *Pairwise annihilation of spinless excitons.* The operators A_j now have the form $a(\mathbf{R})a(\mathbf{R}')$; the quantity μ_{jj} depends only on $\mathbf{R}-\mathbf{R}'$. For the one-particle density matrix we have

$$M = a^\dagger(\mathbf{R})a(\mathbf{R}),$$

and the annihilative part of the equation of motion becomes

$$\left(\frac{\partial}{\partial t}\right)_{\text{ann}} \rho_1(\mathbf{R}) = -\sum_{\mathbf{R}'} 2\,\mathrm{Re}\mu(\mathbf{R}-\mathbf{R}')$$
$$\times\langle a^\dagger(\mathbf{R})a^\dagger(\mathbf{R}')a(\mathbf{R})a(\mathbf{R}')\rangle \equiv -\sum_{\mathbf{R}'} \lambda(\mathbf{R}')\rho_2(\mathbf{R}'). \quad \text{(B12)}$$

For the two-particle density matrix we have

$$M = a^\dagger(\mathbf{R}')a^\dagger(\mathbf{R}'+\mathbf{R})a(\mathbf{R}')a(\mathbf{R}'+\mathbf{R}),$$

and we obtain

$$\left(\frac{\partial}{\partial t}\right)_{\text{ann}} \rho_2(\mathbf{R}) = -\lambda(\mathbf{R})\rho_2(\mathbf{R})$$
$$-\sum_{R'} [\lambda(\mathbf{R}'-\mathbf{R}'')+\lambda(\mathbf{R}'+\mathbf{R}-\mathbf{R}'')]$$
$$\times\langle a^\dagger(\mathbf{R}')a^\dagger(\mathbf{R}'+\mathbf{R})a^\dagger(\mathbf{R}'')a(\mathbf{R}')a(\mathbf{R}'+\mathbf{R})a(\mathbf{R}'')\rangle. \quad \text{(B13)}$$

(*c*) *Pairwise annihilation of triplet excitons.* To describe annihilation in the singlet channel, the interaction V must have the form

$$V = \sum_{n,m,\mathbf{R},\mathbf{R}'} B_s^\dagger(\mathbf{R}-\mathbf{R}')\langle n,m|s\rangle a_n(\mathbf{R})a_m(\mathbf{R}') + \text{H.c.}, \quad \text{(B14)}$$

where $|s\rangle$ is the singlet pair spin state and H.c. denotes that the Hermitian conjugate of the first term is to be added. Accordingly, A_j is to be identified with the combination

$$\sum_{n,m} \langle n,m|s\rangle a_n(\mathbf{R})a_m(\mathbf{R}').$$

Calling $\mathrm{Re}\mu_{jj} = \frac{1}{2}\lambda_s(\mathbf{R}-\mathbf{R}')$, we find the annihilative part of the equation of motion for the one-particle density matrix to be

$$\left(\frac{\partial}{\partial t}\right)_{\text{ann}} \langle n|\rho_1(\mathbf{R})|m\rangle = -\tfrac{1}{2}\sum_{\mathbf{R}'} \lambda_s(\mathbf{R}') \sum_{n',m',l}$$
$$\times\langle n,l|\rho_2(\mathbf{R}')|n',m'\rangle\langle n',m'|s\rangle\langle s|m,l\rangle$$
$$+\langle n,l|s\rangle\langle s|n',m'\rangle\langle n',m'|\rho_2(\mathbf{R}')|m,l\rangle. \quad \text{(B15)}$$

The equation for the two-particle matrix contans terms involving three-particle density matrices, as in Eq. (B13); the term important in the low-density limit is the remaining term which involves only the two-particle density matrix. This term is given by

$$\left(\frac{\partial}{\partial t}\right)_{\text{ann}} \langle n,n'|\rho_2(\mathbf{R})|m,m'\rangle = -\tfrac{1}{2}\lambda_s(\mathbf{R}) \sum_{l,l'}$$
$$\times\langle n,n'|s\rangle\langle s|l,l'\rangle\langle l,l'|\rho_2(\mathbf{R})|m,m'\rangle$$
$$+\langle n,n'|\rho_2(\mathbf{R})|l,l'\rangle\langle l,l'|s\rangle\langle s|m,m'\rangle. \quad \text{(B16)}$$

In the triplet channel we suppose that only one of the two triplets is annihilated in any given annihilation event. The interaction V then has the form

$$V = \sum_{n,m,l,\mathbf{R},\mathbf{R}'} B_T^\dagger(\mathbf{R}-\mathbf{R}')\langle n,m|j\rangle 2^{-1/2}$$
$$\times[a_j^\dagger(\mathbf{R})+a_j^\dagger(\mathbf{R}')]a_n(\mathbf{R})a_m(\mathbf{R}') + \text{H.c.}, \quad \text{(B17)}$$

where $|j\rangle$ is the pair spin state having total spin 1 and quantum number m_s equal to m_s of the single-particle triplet spin state j of the surviving exciton. The surviving exciton is left on either $\mathbf{R}$ or $\mathbf{R}'$ with equal probability. The one-particle density matrix annihilates for this interaction according to the scheme

$$\left(\frac{\partial}{\partial t}\right)_{\text{ann}} \langle n|\rho_1(\mathbf{R})|m\rangle = -\tfrac{1}{2}\sum_{\mathbf{R}'} \lambda_T(\mathbf{R}')\{ \sum_{n',m',l,j}$$
$$\times[\langle n,l|\rho_2(\mathbf{R}')|n',m'\rangle\langle n',m'|j\rangle\langle j|m,l\rangle$$
$$+\langle n,l|j\rangle\langle j|n',m'\rangle\langle n',m'|\rho_2(\mathbf{R})|m,l\rangle]$$
$$-\sum_{n',m',n'',m''} \langle n|n',m'\rangle\langle n',m'|\rho_2(\mathbf{R})|n'',m''\rangle$$
$$\times\langle n'',m''|m\rangle\}, \quad \text{(B18)}$$

while the leading term in the annihilation scheme for the two-particle density matrix is

$$\left(\frac{\partial}{\partial t}\right)_{\text{ann}} \langle nn'|\rho_2(\mathbf{R})|mm'\rangle = -\tfrac{1}{2}\lambda_T(\mathbf{R}) \sum_{l,l',j}$$
$$\times[\langle n,n'|\rho_2(\mathbf{R})|l,l'\rangle\langle l,l'|j\rangle\,\langle j|m,m'\rangle$$
$$+\langle n,n'|j\rangle\langle j|l,l'\rangle\langle l,l'|\rho_2(\mathbf{R})|m,m'\rangle]. \quad \text{(B19)}$$

Equations (B16) and (B19) are precisely of the form (28) of the text, since the projection operators into the singlet and the triplet manifolds of pair spin states are given by, respectively, $P_s = |s\rangle\langle s|$ and $P_T = \sum_j |j\rangle\langle j|$. The triplet annihilation rate $(\frac{1}{2}\gamma n^2)$ is obtained as the spin trace of Eqs. (B15) and (B18) and leads to formulas (31) and (42) of the text. Note the appearance of the factor $\frac{1}{2}$ in the triplet annihilation rate via the triplet channel, resulting from the fact that only one exciton is destroyed in each annihilation event.

APPENDIX C: ANNIHILATION WITH DETAILED SPIN RELAXATION

In this Appendix we examine triplet exciton mutual annihilation in the presence of relaxation which for the one-exciton density matrix takes the form

$$\left(\frac{\partial}{\partial t}\right)_{\text{rel}} \langle n|\rho|m\rangle = -(1-\delta_{nm})\zeta_{nm}^{(2)}\langle n|\rho|m\rangle - \delta_{nm}\Big[\Big(\sum_j \zeta_{jn}^{(1)}\Big)\langle n|\rho|n\rangle - \sum\big(\zeta_{nj}^{(1)}\langle j|\rho|j\rangle\big)\Big]. \tag{C1}$$

Here $|n\rangle$ is a single-exciton spin state which is an eigenstate of the spin Hamiltonian $\mathcal{H}$, with eigenvalue E_n. The scheme (C1) is expected to be applicable whenever all energy differences $E_n - E_m$ are large compared to all relaxation rates.

This scheme must be used whenever the annihilation rate is sensitive to the effective exciton decay rate, e.g., in one-dimensional systems or in two-dimensional systems where spin relaxation is faster than the effective decay rate due to out-of-plane diffusion. Although a framework is established below in terms of which the general problem arising from (C1) could in principle be solved, actual evaluations are performed only when results are relatively insensitive to the spin relaxation rates, so that deviations of such rates from their average can be treated as a perturbation. A further approximation is made by assuming that single-exciton spin state occupation probabilities are nearly equal, even when a nearby exciton is influencing the relative occupation probabilities of the spin states of the pair. The error introduced via this assumption is, however, estimated to be small for most conditions.

In order to generalize (C1) for a pair density matrix, we have to choose a basis of pair states $|n,n'\rangle \equiv |n\rangle|n'\rangle$ which consists of products of single-particle stationary states. If we furthermore ignore correlated spin relaxation, i.e., relaxation of the spin of one exciton induced by the presence of another nearby exciton, then the relaxation of the pair density matrix ρ_2 can be characterized by

$$\left(\frac{\partial}{\partial t}\right)_{\text{rel}} \langle n,n'|\rho_2|m,m'\rangle = -\big[(1-\delta_{nm})\zeta_{nm}^{(2)} + (1-\delta_{n'm'})\zeta_{n'm'}^{(2)}\big]\langle n,n'|\rho_2|m,m'\rangle - \delta_{nm}\Big[\sum_j \zeta_{jn}^{(1)}\langle n,n'|\rho_2|n,m'\rangle - \sum \zeta_{nj}^{(1)}\langle j,n'|\rho_2|j,m'\rangle\Big] - \delta_{n'm'}\Big[\sum_j \zeta_{jn'}^{(1)}\langle n,n'|\rho_2|m,n'\rangle - \sum_j \zeta_{n'j}^{(1)}\langle n,j|\rho_2|m,j\rangle\Big]. \tag{C2}$$

Expression (C2) is almost certainly incorrect for exciton separations of the order of a lattice spacing, where correlated relaxation can become important. The neglect of such correlated relaxation terms can, however, be justified by an argument similar to that used for neglecting the exciton-exciton interaction $V(\mathbf{R})$. Like that interaction, the correlated relaxation terms are also short range. All we need is that these terms be small compared to the annihilation rate $\Lambda(\mathbf{R})$.

Let us add the terms (C2) to the appropriate matrix element of the equation of motion, Eq. (30). We neglect the interaction $V(\mathbf{R})$ at the outset. The procedure for solving the resulting equation involves, as before, the solution of the long-range problem via a Green's function analogous to (35), expressing each matrix element formally in terms of short-range terms, as in Eq. (36), and some sort of approximate solution of the finite number of equations involving the short-range quantities. In order to follow this procedure, it is essential that the equation of motion can be separated into equations whose long-range behavior has the form of the right-hand member of Eq. (35). The separation is automatic for the off-diagonal terms $n \neq m$, $n' \neq m'$. The formal solution analogous to (36) is

$$\langle n,n'|\rho_2(\mathbf{R})|m,m'\rangle = g\big[\mathbf{R}, \beta + \tfrac{1}{2}(\zeta_{nm}^{(2)} + \zeta_{n'm'}^{(2)}) + \tfrac{1}{2}i(E_n + E_{n'} - E_m - E_{m'})\big]\sum_{\mathbf{R}'} \Psi(\mathbf{R}')\langle n,n'|\rho_2(\mathbf{R}')|m,m'\rangle + \sum_{\mathbf{R}'} g\big[\mathbf{R}-\mathbf{R}', \beta + \tfrac{1}{2}(\zeta_{nm}^{(2)} + \zeta_{n'm'}^{(2)}) + \tfrac{1}{2}i(E_n + E_{n'} - E_m - E_{m'})\big]\big[-\Psi(\mathbf{R}')\langle n,n'|\rho_2(\mathbf{R}')|m,m'\rangle + \tfrac{1}{4}\langle n,n'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}') + \rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|m,m'\rangle\big]. \tag{C3}$$

The terms diagonal in one particle ($n = m$ or $n' = m'$) or in both particles must be dealt with in several steps. First, we consider the spin trace of the equation of motion. This is the same as the spin trace of (30), since the trace of (C2) vanishes; the result is given in Eq. (50). Next, we find the equation of motion for the partial spin trace of the pair density matrix, with respect to spin variables of only one member of the exciton pair. The spin relaxation part of this equation has the form (C1), with the symbol ρ replaced by an appropriate one-particle trace of ρ_2. The off-diagonal terms each decay at their individual rates, and we have (for $n\neq m$)

$$\sum_{n'} \langle n,n'|\rho_2(\mathbf{R}')|m,n'\rangle = g[\mathbf{R}, \beta+\tfrac{1}{2}\zeta_{nm}^{(2)}+\tfrac{1}{2}i(E_n-E_m)] \sum_{\mathbf{R}'} \sum_{n'} \Psi(\mathbf{R}')\langle nn'|\rho_2(\mathbf{R}')|mn'\rangle$$
$$+\sum_{\mathbf{R}'} g[\mathbf{R}-\mathbf{R}', \beta+\tfrac{1}{2}\zeta_{nm}^{(2)}+\tfrac{1}{2}i(E_n-E_m)][-\Psi(\mathbf{R}') \sum_{n'} \langle nn'|\rho_2(\mathbf{R}')mn'\rangle$$
$$+\tfrac{1}{4}\sum_{n'} \langle nn'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|mn'\rangle]. \quad \text{(C4)}$$

The equations for the diagonal terms of the partial trace are coupled and have the constraint that their sum (the complete trace) must satisfy (50). The latter difficulty is removed by considering instead the equations for the correlation functions

$$f_{nm}(\mathbf{R}) \equiv \sum_{n'} \langle nn'|\rho_2(\mathbf{R})|mn'\rangle - \tfrac{1}{3}\,\mathrm{Tr}\rho_2(\mathbf{R})\delta_{nm}. \quad \text{(C5)}$$

The equations for f_{nn} are still coupled, but can in principle be uncoupled by choosing linear combinations of the diagonal terms which relax independently of one another. The long-range behavior for each such linear combination can then be solved for. If the decay rates $\zeta_i^{(1)}$ of these linear combinations are all nearly equal, such that at least the quantities $g(\mathbf{R}, \beta+\frac{1}{2}\zeta_i^{(1)})$ can be approximated as being equal, the result is the same as would have been obtained had we initially replaced all $\zeta_{nm}^{(1)}$ by an average value, conveniently called $\frac{1}{3}\zeta^{(1)}$. We henceforth consider only cases where such an approximation is applicable. The expression for $f_{nn}(\mathbf{R})$ is then

$$f_{nn}(\mathbf{R}) = g(\mathbf{R}, \beta+\tfrac{1}{2}\zeta^{(1)}) \sum_{R'} \Psi(\mathbf{R}')f_{nn}(\mathbf{R}') + \sum_{\mathbf{R}'} g(\mathbf{R}-\mathbf{R}', \beta+\tfrac{1}{2}\zeta^{(1)})[-\Psi(\mathbf{R}')f_{nn}(\mathbf{R}')$$
$$+\tfrac{1}{4}\sum_{n'} \langle nn'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|nn'\rangle - \tfrac{1}{12}\sum_{l,n'} \langle ln'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|ln'\rangle]. \quad \text{(C6)}$$

We are at last in a position to find an expression for the remaining matrix elements of the pair density matrix, which now have the constraints (C6), (50), and (C4) imposed upon certain of their sums. The constraints are eliminated by considering the two-particle correlation function

$$f_{nm;n'm'}^{(2)}(\mathbf{R}) \equiv \langle nn'|\rho_2(\mathbf{R})|mm'\rangle - \tfrac{1}{3}\delta_{nm}f_{n'm'}(\mathbf{R}) - \tfrac{1}{3}\delta_{n'm'}f_{nm}(\mathbf{R}) - \tfrac{1}{9}\delta_{nm}\delta_{n'm'}\,\mathrm{Tr}\rho_2(\mathbf{R}). \quad \text{(C7)}$$

We find, with the assumption of nearly equal diagonal relaxation rates,

$$f_{nn;n'n'}^{(2)}(\mathbf{R}) = g(\mathbf{R}, \beta+\zeta^{(1)}) \sum_{\mathbf{R}'} \Psi(\mathbf{R}')f_{nn;n'n'}^{(2)}(\mathbf{R}') + \sum_{\mathbf{R}'} g(\mathbf{R}-\mathbf{R}', \beta+\zeta^{(1)})[-\Psi(\mathbf{R}')f_{nn;n'n'}^{(2)}(\mathbf{R}')$$
$$+\tfrac{1}{4}\langle nn'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|nn'\rangle - \tfrac{1}{12}\sum_{l} \langle nl|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|nl\rangle$$
$$-\tfrac{1}{12}\sum_{l} \langle ln'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|ln'\rangle + (1/36)\sum_{l,l'} \langle ll'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|ll'\rangle], \quad \text{(C8)}$$

and, for $n\neq m$,

$$f_{nm;n'n'}(\mathbf{R}) = g[\mathbf{R}, \beta+\tfrac{1}{2}(\zeta^{(1)}+\zeta_{nm}^{(2)})+\tfrac{1}{2}i(E_n-E_m)]\sum_{\mathbf{R}'} \Psi(\mathbf{R}')f_{nm;n'n'}(\mathbf{R}')$$
$$+\sum_{\mathbf{R}'} [g(\mathbf{R}-\mathbf{R}', \beta+\tfrac{1}{2}(\zeta^{(1)}+\zeta_{nm}^{(2)})+\tfrac{1}{2}i(E_n-E_m)][-\Psi(\mathbf{R}')f_{nm;n'm'}(\mathbf{R}')+\tfrac{1}{4}\langle nn'|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|mn'\rangle$$
$$-\tfrac{1}{12}\sum_{l} \langle nl|\Lambda(\mathbf{R}')\rho_2(\mathbf{R}')+\rho_2(\mathbf{R}')\Lambda(\mathbf{R}')|ml\rangle]. \quad \text{(C9)}$$

In order to calculate the annihilation rate, one would have to solve the simultaneous equations (C3), (50), (C4), (C6), (C8), and (C9) for as many **R**'s as either $\Psi(\mathbf{R})$ or $\Lambda(\mathbf{R})$ is nonvanishing. This task is difficult even within the smooth approximation. The solution in the smooth approximation can be expressed in the form

$$\begin{aligned}\langle n,n'|\rho_2(\bar{R})|m,m'\rangle &= \tfrac{1}{4}G[\beta+\tfrac{1}{2}(\zeta_{nm}+\zeta_{n'm'})+\tfrac{1}{2}i(E_n+E_{n'}-E_m-E_{m'})]\langle n,n'|M|m,m'\rangle \\ &+\tfrac{1}{12}\delta_{nm}\{G[\beta+\tfrac{1}{2}\zeta_{n'm'}+\tfrac{1}{2}i(E_{n'}-E_{m'})]-G[\beta+\tfrac{1}{2}(\zeta_{n'n}+\zeta_{n'm'})+\tfrac{1}{2}i(E_{n'}-E_{m'})]\}\sum_l \langle l,n'|M|l,n'\rangle \\ &+\tfrac{1}{12}\delta_{n'm'}\{G[\beta+\tfrac{1}{2}\zeta_{nm}+\tfrac{1}{2}i(E_n-E_m)]-G[\beta+\tfrac{1}{2}(\zeta_{nn}+\zeta_{nm})+\tfrac{1}{2}i(E_n-E_m)]\}\sum_l \langle n,l|M|m,l\rangle \\ &+\delta_{nm}\delta_{n'm'}\{(\tfrac{1}{3}nv)^2+(1/36)[G(\beta)+G(\beta+\zeta_{nn})-2G(\beta+\tfrac{1}{2}\zeta_{nn})]\sum_{l,l'}\langle l,l'|M|l,l'\rangle, \qquad \text{(C10)}\end{aligned}$$

where we have defined $\zeta_{nm}\equiv\zeta_{nm}{}^{(2)}$ for $n\neq m$, $\zeta_{nn}\equiv\zeta^{(1)}$, $M\equiv\Lambda\rho_2(\bar{R})+\rho_2(\bar{R})\Lambda$, and where the function G has been defined in (38).

The expression becomes considerably more manageable if all single-exciton spin states are equally probable, so that

$$\sum_l \langle n,l|\rho_2(\bar{R})|m,l\rangle=\tfrac{1}{3}\delta_{nm}\sum_{l,l'}\langle l,l'|\rho_2(\bar{R})|l,l'\rangle. \qquad \text{(C11)}$$

We expect (C11) to hold at least approximately, since only relative spin orientations of the annihilating exciton pair affect the annihilation process. We proceed by assuming (C11); an estimate of the error introduced thereby will be made subsequently. The condition (C11) implies, via (C4) and (C6), the relation

$$\sum_l \langle l,n|M|l,m\rangle=\tfrac{1}{3}\delta_{nm}\sum_{ll'}\langle l,l'|M|l,l'\rangle, \qquad \text{(C12)}$$

which eliminates the most troublesome terms in (C10); the expression for the density matrix becomes

$$\begin{aligned}\langle n,n'|\rho_2(\bar{R})|m,m'\rangle &= \tfrac{1}{4}G[\beta+\tfrac{1}{2}(\zeta_{nm}+\zeta_{n'm'})+\tfrac{1}{2}i(E_n+E_{n'}-E_m-E_{m'})]\langle n,n'|M|m,m'\rangle \\ &+\delta_{nm}\delta_{n'm'}\{(\tfrac{1}{3}nv)^2+(1/36)[G(\beta)-G(\beta+\zeta_{nn})]\sum_{l,l'}\langle l,l'|M|l,l'\rangle\} \\ &\equiv\tfrac{1}{4}G_{nn'mm'}\langle n,n'|M|m,m'\rangle+(\tfrac{1}{3}nv)^2c\delta_{nm}\delta_{n'm'}. \qquad \text{(C13)}\end{aligned}$$

Let us express (C13) in terms of either even or odd spin states. We define

$$\begin{aligned}&|n,m,\pm\rangle=2^{-1/2}(|n,m\rangle\pm|m,n\rangle) \quad \text{for} \quad m\neq n, \\ &|n,n,+\rangle=|n,n\rangle, \\ &|n,n,-\rangle=0, \qquad \text{(C14)} \\ &G_{nn'mm'}{}^{\pm}=\tfrac{1}{2}(G_{nn'mm'}\pm G_{n'nmm'}),\end{aligned}$$

and make use of the property

$$\begin{aligned}\langle n,n'|\rho_2(\mathbf{R})|m,m'\rangle &= \langle n',n|\rho_2(-\mathbf{R})|m',m\rangle \\ &= \langle n',n|\rho_2(\mathbf{R})|m',m\rangle, \qquad \text{(C15)}\end{aligned}$$

where the first equality arises from the indistinguishability of the two excitons of the pair, while the second holds only if all terms in the equation of motion are invariant under spatial inversion, a property we shall assume. Equation (C13) becomes

$$\begin{aligned}\langle n,n',\pm|\rho_2(\bar{R})|m,m',\pm\rangle &= (\tfrac{1}{3}nv)^2c\delta_{nm}\delta_{n'm'} \\ &+\tfrac{1}{4}[G_{nn'mm'}{}^{+}\langle n,n',\pm|M|m,m',\pm\rangle \\ &+G_{nn'mm'}{}^{-}\langle n,n',\mp|M|m,m',\mp\rangle]. \qquad \text{(C16)}\end{aligned}$$

It will be recalled that the matrix Λ, when operating on odd spin states, is equal to the constant λ_T, so that

$$\langle n,n',-|M|m,m',-\rangle=\lambda_T\langle n,n',-|\rho_2(\bar{R})|m,m',-\rangle. \qquad \text{(C17)}$$

With the aid of (C17), the odd matrix elements can be eliminated from (C16). Let us abbreviate $|n,n',+\rangle\equiv|l\rangle$, and write, e.g., $G_{nn'mm'}=G_{ll'}$. The resulting equation then is

$$\begin{aligned}\langle l|\rho_2(\bar{R})|l'\rangle &= \delta_{ll'}(\tfrac{1}{3}nv)^2cF_{1ll} \\ &+\tfrac{1}{4}\lambda_S F_{2ll'}\sum_{l''}[\langle l|S\rangle\langle S|l''\rangle\langle l''|\rho_2(\bar{R})|l'\rangle \\ &+\langle l|\rho_2(\bar{R})|l''\rangle\langle l''|S\rangle\langle S|l'\rangle], \qquad \text{(C18)}\end{aligned}$$

where

$$\begin{aligned}F_{1ll}&\equiv1+\tfrac{1}{2}\lambda_T G_{ll}{}^{-}/(1-\tfrac{1}{2}\lambda_T G_{ll}{}^{+}), \\ F_{2ll'}&\equiv G_{ll'}{}^{+}+\tfrac{1}{2}\lambda_T(G_{ll'}{}^{-})^2/(1-\tfrac{1}{2}\lambda_T G_{ll'}{}^{+}).\end{aligned}$$

The simultaneous equations (C18) have essentially the same form as Eq. (41), except for the fact that the quantity c depends on the solution. The equation can be simplified by the same trick used in simplifying (41), provided we eliminate c from the equations. To do so, we define

$$A_l=(\tfrac{1}{3}nv)^{-2}c^{-1}\langle l|S\rangle\sum_{l'}\langle S|l'\rangle\langle l'|\rho_2(\bar{R})|l\rangle \qquad \text{(C19)}$$

and obtain the equation

$$\begin{aligned}&[1-\tfrac{1}{4}\lambda_S\sum_{l'}|\langle S|l'\rangle|^2F_{2ll}]A_l \\ &\qquad=|\langle S|l\rangle|^2[F_{1ll}+\tfrac{1}{4}\lambda_S\sum_{l'}F_{2ll'}A_{l'}{}^*]. \qquad \text{(C20)}\end{aligned}$$

Define the quantities

$$A_S=\sum_l A_l \tag{C21}$$

and

$$A_T=\sum_{(l)}\frac{1+\frac{1}{4}G_{ll}^- A_l}{1-\frac{1}{2}\lambda_T G_{ll}^+}, \tag{C22}$$

where (l) indicates that the sum is restricted to pair states l which are products of two distinct single-particles states.

In terms of these quantities, the coefficient c is given by

$$c=1/\{1-\tfrac{1}{2}[G(\beta)-G(\beta+\zeta_{nn})][\lambda_S A_S+\lambda_T A_T]\} \tag{C23}$$

and the annihilation rate constants in the singlet and triplet channels are

$$\gamma_S=(v\lambda_S/9)cA_S,\quad \gamma_T=(v\lambda_T/18)cA_T. \tag{C24}$$

Finally, we estimate the error introduced by the approximation (C11). For this purpose, we may use the results of the text for a constant spin relaxation rate and look only at the soluble limit of large pair energy separations. In this limit the pair density matrix is given for even states by

$$\langle l|\rho_2(\bar{R})|l\rangle=c(\tfrac{1}{3}nv)^2/[1+k|\langle S|l\rangle|^2] \tag{C25a}$$

or

$$\langle n,m,+|\rho_2(\bar{R})|n,m,+\rangle =c(\tfrac{1}{3}nv)^2/[1+k|\langle S|n,m\rangle|^2(2-\delta_{nm})], \tag{C25b}$$

where

$$k=-\tfrac{1}{2}\lambda_S G(\beta+\zeta),$$

and for the odd states by

$$\langle n,m,-|\rho_2(\bar{R})|n,m-\rangle=c(\tfrac{1}{3}nv)^2/ [1-\tfrac{1}{2}\lambda_T G(\beta+\zeta)]. \tag{C26}$$

The quantities f_{nn} are then calculated via (C14) and the definition (C5). The result is

$$f_{nn}=-(\tfrac{1}{3}nv)^2 c(B_n-\tfrac{1}{3}\sum_m B_m),$$

where

$$B_n\equiv\sum_m\frac{k|\langle S|n,m\rangle|^2}{1+k|\langle S|n,m\rangle|^2(2-\delta_{nm})}. \tag{C27}$$

The relative error in the singlet part of γ, $\delta\gamma_S/\gamma_S$, due to nonvanishing f_{nn}, is calculated to be

$$\delta\gamma_S/\gamma_S=-\tfrac{2}{3}\{1-[G(\beta+\zeta)/G(\beta+\tfrac{1}{2}\zeta)]\} \times\sum_n(B_n-\tfrac{1}{3}\sum_m B_m)^2/\sum_m B_m. \tag{C28}$$

We get an upper limit on (C28) as follows. The singlet amplitudes $\langle S|n,m\rangle$ are restricted by the identity

$$\sum_m|\langle S|n,m\rangle|^2=\tfrac{1}{3}. \tag{C29}$$

This identity is easily proved by noting that the left-hand side of (C29) is basis independent. Evaluating it in a convenient basis of triplet states gives $\frac{1}{3}$. Subject to (C29), the quantities B_n have the permissible range

$$k/(3+2k)\leq B_n\leq 2k/(6+k). \tag{C30}$$

The range (C30) determines an upper limit on (C28), which is found to be

$$|\delta\gamma_S/\gamma_S|\leq(1/81)\{1-[G(\beta+\zeta)/G(\beta+\tfrac{1}{2}\zeta)]\} \times k^3(1+\tfrac{1}{6}k)^{-2}(1+\tfrac{2}{3}k)^{-1}. \tag{C31}$$

The factor in curly brackets will be small whenever ζ is small compared to β. Moreover, it will generally be small in three- and two-dimensional systems where the dependence of G on the total effective lifetime is weak. The remaining multiplicand will also be small compared to unity whenever $k\lesssim 1$.

APPENDIX D: THEORY OF SPIN RELAXATION VIA EXCITON HOPPING BETWEEN INEQUIVALENT SITES

In this Appendix we compute the spin relaxation rates of triplet excitons in anthracene at room temperature with the aid of the known crystal structure, spin Hamiltonian, and exciton hopping rates. The general theory is applicable to triplet excitons in any molecular crystal with two molecules per unit cell, provided exciton motion can be described by means of a hopping model.

We denote by $\mathcal{H}_A$ and $\mathcal{H}_B$ the Hamiltonians associated with each of the two inequivalent molecules of the anthracene lattice. The actual spin Hamiltonian at the lattice point $\mathbf{R}$ can then be expressed as

$$\mathcal{H}(\mathbf{R})=\tfrac{1}{2}(\mathcal{H}_A+\mathcal{H}_B)+\tfrac{1}{2}(\mathcal{H}_A-\mathcal{H}_B)\exp(\tfrac{1}{2}i\mathbf{G}\cdot\mathbf{R}) \equiv\mathcal{H}+h\exp(\tfrac{1}{2}i\mathbf{G}\cdot\mathbf{R}), \tag{D1}$$

where $\mathbf{G}$ is the reciprocal lattice vector $\mathbf{G}=4\pi\mathbf{b}/b^2$. Equation (D1) reduces to $\mathcal{H}_A$ at lattice points equivalent to $\mathbf{R}=0$, and to $\mathcal{H}_B$ otherwise. $\mathcal{H}$ is the Hamiltonian used in (58). The equation of motion for the one-exciton density matrix $\rho(\mathbf{R})$ is, in the hopping model,

$$\frac{\partial}{\partial t}\rho(\mathbf{R})=i[\mathcal{H}(\mathbf{R}),\rho(\mathbf{R})]+\sum_{\mathbf{R}'}\Psi(\mathbf{R}-\mathbf{R}')\rho(\mathbf{R}') -\sum_{\mathbf{R}'}\Psi(\mathbf{R}')\rho(\mathbf{R}). \tag{D2}$$

We seek approximations which reduce Eq. (D2) to a form containing only $\mathcal{H}$ and a relaxation term in the form (C1). The procedure is essentially the same as that employed by Kubo and Tomita[35] in calculating motional relaxation, the only difference being the fact that the fields inducing the relaxation now have definite orientations in space. The reduction is effected by

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[35] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

means of the matrix quantities

$$\eta(\mathbf{k},\omega)\equiv\int_{-\infty}^{\infty} dt\, e^{i\omega t}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\mathcal{H}t}\rho(\mathbf{R},t)e^{-i\mathcal{H}t}, \tag{D3}$$

which satisfy the equation

$$[-i\omega+f(\mathbf{k})]\eta(\mathbf{k},\omega)=-i(2\pi)^{-1}\times\int_{-\infty}^{\infty} d\omega'\,[h(\omega'),\,\eta(\mathbf{k}+\tfrac{1}{2}\mathbf{G},\,\omega-\omega')], \tag{D4}$$

where

$$h(\omega)\equiv\int_{-\infty}^{\infty} dt\, e^{i\omega t}e^{i\mathcal{H}t}he^{-i\mathcal{H}t}$$

and

$$f(\mathbf{k})\equiv\sum_{\mathbf{R}}\Psi(\mathbf{R})(1-e^{-i\mathbf{k}\cdot\mathbf{R}}).$$

If we iterate Eq. (D4) once and evaluate the matrix elements of the result in a basis which diagonalizes the average Hamiltonian $\mathcal{H}$, such that $\langle n|\mathcal{H}|m\rangle=E_n\delta_{nm}$, we obtain

$$\begin{aligned}[-i\omega+f(\mathbf{k})]\langle n|\eta(\mathbf{k},\omega)|m\rangle
&=-\sum_{n',m'}\frac{\langle n|h|n'\rangle[\langle n'|h|m'\rangle\langle m'|\eta(\mathbf{k},\,\omega+E_n-E_{m'})|m\rangle-\langle n'|\eta(\mathbf{k},\,\omega+E_n-E_{n'}+E_{m'}-E_m)|m'\rangle\langle m'|h|m\rangle]}{-i(\omega+E_n-E_{n'})+f(\mathbf{k}+\frac{1}{2}\mathbf{G})}\\
&\quad+\frac{[\langle n|\eta(\mathbf{k},\,\omega+E_{n'}-E_m)|n'\rangle\langle n'|h|m'\rangle-\langle n|h|n'\rangle\langle n'|\eta(\mathbf{k},\,\omega+E_n-E_{n'}+E_{m'}-E_m)|m'\rangle]\langle m'|h|m\rangle}{-i(\omega+E_{m'}-E_m)+f(\mathbf{k}+\frac{1}{2}\mathbf{G})},
\end{aligned} \tag{D5}$$

where we have used the property that $\mathbf{k}+\mathbf{G}$ is equivalent to $\mathbf{k}$. Equation (D5) is still exact. Let us look at this equation in the small-$\mathbf{k}$ limit. The justification for so doing is that we are primarily interested in the long-range spatial behavior of the density matrix, for we have seen that most of the essential features of exciton-exciton annihilation are governed by the long-range behavior. For $\mathbf{k}$ near the center of the Brillouin zone, $f(\mathbf{k})\approx Dk^2$ and can be made arbitrarily small. Now $\eta(\mathbf{k},\omega)$ becomes small for large ω, with a half-width roughly $f(\mathbf{k})+\zeta$, where ζ is an average relaxation rate as yet to be computed. Let us look at (D5) for $\omega\lesssim f(\mathbf{k})+\zeta$, and let us suppose that $f(\mathbf{k})+\zeta\ll f(\mathbf{k}+\frac{1}{2}G)\approx f(\frac{1}{2}G)$. If we can arrange it that all nonzero energy differences occurring in (D5) are large compared to $f(\mathbf{k})+\zeta$, we can neglect all those terms in which $\eta(\mathbf{k},\omega)$ has as its argument a nonzero energy difference. If furthermore there are no energy degeneracies as well as no pair energy degeneracies, then (D5) simplifies to the approximate form

$$\begin{aligned}[-i\omega+f(\mathbf{k})]\langle n|\eta(\mathbf{k},\omega)|m\rangle
&=-i(E_n-E_m)\langle n|\eta(\mathbf{k},\omega)|m\rangle\\
&\quad-(1-\delta_{nm})\zeta_{nm}{}^{(2)}\langle n|\eta(\mathbf{k},\omega)|m\rangle\\
&\quad-\delta_{nm}[(\sum_j\zeta_{jn}{}^{(1)})\langle n|\eta(\mathbf{k},\omega)|n\rangle\\
&\qquad-\sum_j(\zeta_{nj}{}^{(1)}\langle j|\eta(\mathbf{k},\omega)|j\rangle)],
\end{aligned} \tag{D6a}$$

where

$$\epsilon_n=\sum_{n'}\frac{(E_n-E_{n'})|\langle n|h|n'\rangle|^2}{f(\frac{1}{2}\mathbf{G})^2+(E_n-E_{n'})^2}, \tag{D6b}$$

$$\zeta_{nm}{}^{(2)}=\sum_{n'}\frac{f(\frac{1}{2}\mathbf{G})|\langle n|h|n'\rangle|^2}{f(\frac{1}{2}\mathbf{G})^2+(E_n-E_{n'})^2}+\sum_{m'}\frac{f(\frac{1}{2}\mathbf{G})|\langle m|h|m'\rangle|^2}{f(\frac{1}{2}\mathbf{G})^2+(E_m-E_{m'})^2}-\frac{2\langle n|h|n\rangle\langle m|h|m\rangle}{f(\frac{1}{2}\mathbf{G})}, \tag{D6c}$$

and

$$\zeta_{nj}{}^{(1)}=\frac{2f(\frac{1}{2}\mathbf{G})|\langle n|h|j\rangle|^2}{f(\frac{1}{2}\mathbf{G})^2+(E_n-E_j)^2}. \tag{D6d}$$

It is not hard to see that, upon substitution of (D3) into (D6a), an equation for $\rho(\mathbf{R},t)$ results which exhibits a relaxation term of precisely the type (C1), with relaxation rates given by (D6c) and (D6d). There are also corrections to the Hamiltonian, resulting in the change of each energy level by an amount ϵ_n. These corrections must be small compared to all zero-order energy differences if the assumptions made in deriving (D6a) are to be valid.

For anthracene, assuming Ψ_b and Ψ_d are the only significant hopping rates, the quantity $f(\frac{1}{2}\mathbf{G})$ is just $8\Psi_d$. The matrix h can be put into the form

$$h=E'(S_{x'}{}^2-S_{y'}{}^2), \tag{D7}$$

where for anthracene we find $E'/g\mu_B=255$ Oe, while the principal axes x', y', z' have the direction cosines, with respect to the axes a, b, and c^*, as follows:

x':	0.656	0.707	0.263,
y':	−0.656	0.707	−0.263,
z':	−0.372	0	0.928.

An upper limit on all relaxation rates is obtained by setting all energy differences in (D6c) and (D6d) equal to zero. This limit is even realizable in practice, since $8\Psi_d$, converted to units of Oe, using $g=2.0$,[29] has the value

$$8\Psi_d\hbar/(2\mu_B)=18\,600\text{ Oe}, \tag{D8}$$

which not only is well above the energy level differences at zero external field, but is even large compared to typical values of the external field in actual experiments.[17,23] In the limit where all energy differences are small compared to (D8), we have

$$\zeta_{nm}{}^{(2)}=[\langle n|h^2|n\rangle+\langle m|h^2|m\rangle-2\langle n|h|n\rangle \times\langle m|h|m\rangle]/8\Psi_d, \tag{D9a}$$

$$\zeta_{nj}{}^{(1)}=2|\langle n|h|j\rangle|^2/8\Psi_d. \tag{D9b}$$

The relaxation rates $\zeta_{nm}{}^{(2)}$ as well as the total diagonal relaxation rates $\sum_j \zeta_{nj}{}^{(1)}$ are all seen to be bounded from above by the maximum value attainable by the quantity $\langle n|h^2|m\rangle/4\Psi_d$. Since $h^2=(E')^2S_{z'}{}^2$, this maximum value is $(E')^2/4\Psi_d$, which in units of Oe is about 6 Oe. Except near degeneracies, this value is indeed well below all finite energy differences. Similarly, the energy corrections ϵ_n are smaller than typical energy differences by at least a factor $(E'/8\Psi_d)^2\approx 2\times10^{-4}$. Thus the assumptions leading to (D6a) are justified, provided there are no near degeneracies and provided Dk^2 is small compared to all finite energy differences. The k's of interest will necessarily correspond to distances of the order of a diffusion length, $(D/\zeta)^{1/2}$, where ζ is a typical relaxation rate. Thus Dk^2 is of the order of ζ and is sufficiently small. Finally, the small magnitude of the relaxation rates allows us to ignore near degeneracies: Such degeneracies will modify the relaxation rates at worst only when the corresponding energy difference becomes comparable to 6 Oe, in appropriate units, a very narrow energy range compared to the full range. Nor do such modifications significantly affect the resonance shapes; the resonance shapes will be affected only in a range of at most 6 Oe about the center of the resonance; by contrast, the resonance width will be of the order of $2.24(\zeta\Psi_d)^{1/2}\approx|E'|\sim 250$ Oe, even when relaxation is the only decay mechanism.

For external fields well below the value (D8), the average diagonal relaxation rate is given by

$$\zeta=\tfrac{1}{3}\sum_n\Big(\sum_j \zeta_{nj}{}^{(1)}\Big)=(E')^2/6\Psi_d$$

$$=8.2\times10^7\text{ sec}^{-1}\quad(\hbar\zeta/2\mu_B=4.65\text{ Oe}). \tag{D10}$$

This is also approximately the average of the off-diagonal relaxation rates. If the expression (D9a) is averaged over all n, m, ignoring the restriction $n\neq m$, the result is precisely (D10).

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Optical Nonlinear Susceptibilities: Accurate Relative Values for Quartz, Ammonium Dihydrogen Phosphate, and Potassium Dihydrogen Phosphate

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A complete theoretical and experimental analysis of the Maker fringes leads to the determination of accurate relative nonlinear optical susceptibilities in SiO_2, $NH_4H_2PO_4$, and KH_2PO_4: $d_{11}{}^{2\omega}(SiO_2)=(0.77\pm0.04)\,d_{36}{}^{2\omega}(KH_2PO_4)$; $d_{36}{}^{2\omega}(NH_4H_2PO_4)=(1.21\pm0.05)d_{36}{}^{2\omega}(KH_2PO_4)$, for a fundamental wavelength 1.064 μm. Application of this analysis to earlier data leads to corrected values in good agreement with the present study, thereby establishing these materials as accurate and reliable standards for measurement of nonlinear optical susceptibilities.

INTRODUCTION

Since it is extremely difficult to make accurate absolute-intensity measurements, the components of the tensor describing optical second-harmonic generation or parametric processes have with few exceptions been determined by relative measurements: the elements of the unknown tensor being compared to those of a well-known "standard" material, such as KH_2PO_4 (KDP). Accurate absolute values can then be easily deduced from relative data, provided the standard has been carefully calibrated.

A survey of all the published measurements[1] indicates, however, a complex and quite paradoxical situation. Most importantly, no one material has been chosen as a common standard. Depending on the spectral range (visible, infrared, ultraviolet) and on the techniques

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