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Role of Rate Equations in the Theory of Luminescent Energy Transfer

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In this paper we derive from first principles, equations describing the kinetics of luminescent transfer. We apply the Pauli equation to an appropriately defined density matrix to derive, under one formalism but under opposite limiting assumptions, both the usual nonlinear kinetic rate equations and the equations which form the starting point for the calculations of Forster and others. The transition probabilities entering these equations are discussed. It is shown that they permit multiparticle processes, with great increase in the possibility for resonances that exist if only two-particle processes are considered. Further, in the rate-equation approximation, the concentration dependence of the transition probabilities and of the yield reflects only the number of particles participating in one energy-conserving transfer, and is not associated with the spatial dependence of the interaction. Such an association does exist in the Forster approximation, but a direct correspondence between powers of concentration and multipole orders appears valid only under severe constraints. The observed nonlinearities of decays and of yields, and dependences on the excitation mode, are easily handled with rate equations. Some of the experimental evidence that the rate-equation approximation applies, in fact, to many systems, particularly to rare earths in inorganic hosts, is briefly discussed.

I. INTRODUCTION

The theory of luminescent transfer has been developed by many authors[1-26] over a long period of time. From the copious experimental investigations we cite a sample of those in which yield and decay characteristics have been studied in their quantitative and functional dependence on concentration and other factors.[27-95] Since the problem of fluorescence transfer and quenching first appeared in the context of the kinetics of organic molecules, the interactions initially considered were contact potentials.[1] Forster[2-6] established the role of long-range potentials and the resonant nature of the process. Dexter[7-10] applied the concept of resonant luminescent transfer to impurity systems in inorganic materials. He associated the resonance condition with observable overlap between fluorescent absorption and emission bands; he showed that the interaction potential could usefully be expanded in multipoles, but that this multipole series converges much more slowly than for radiation; he investigated the concentration dependence of transfer and showed that even dilute concentrations could be effective, and he placed cooperative energy absorption within the same framework. There remain certain ambiguities in Dexter's discussion of the concentration dependence of transfer, however, and their resolution will be one of the results of this paper. Colbow[16,18] and Inokuti and Hirayama[17] explicitly treated exchange interactions. The effect of phonons on transfer has also come under scrutiny.[14,23,26] Much effort has gone into finding experimental evidence for specific terms in the interaction potential. Usually one attempts to infer the coordinate dependence of the interaction from the concentration dependence of the decay or of the yield. On the other hand, in studies using rate equations to interpret the data, the multipole question is absent. It is also a curious fact that the concentration dependence follows a square law in the vast majority of cases (though powers up to three are not uncommon), and this is true even where the relevant transitions are high-order forbidden. There has not yet appeared a thoroughgoing attempt to assess the effects of the nonlinear nature of the process.

To resolve these problems we derive in this paper the theoretical apparatus for luminescent transfer, from first principles. The starting equations in previous treatments[2-9,16-18,20] are the final result of our main calculation. The assumptions underlying these equations and the results derived from them, their region of validity, and their relationship to each other come into clear perspective in this fashion. We also derive a number of new results.

In Sec. II we derive an equation for the time development of a fine-grained probability density of the population of single-particle states. We define the ensembles appropriate to the luminescence problem, and then avail ourselves of the density matrix formalism. We briefly review the assumptions implicit in the Pauli equation for the time development of the density matrix. We transform the Pauli equation, whose variables are occupation numbers, into an equation with particle coordinates as variables. In this way we obtain an equation for the time dependence of the fine-grained probability density. We also examine the assumptions implicit in configuration averaging. In Sec. III we derive the usual kinetic nonlinear rate equations, from the results of Sec. II. This is possible under certain limiting assumptions. We also derive the equations used by Forster, Colbow, and Inokuti and Hirayama (FCIH) as their starting point in their calculations. These require, in essence, the opposite limiting assumptions. In Sec. IV we examine in more detail the transition probability that enters into the equations. Among other results, we find that multiparticle processes are highly probable in certain circumstances, and that the concentration dependence of the transition probability reflects the number of interacting particles and not the spatial dependence of the interaction. In Sec. V we analyze the experimental quantity called fluorescent yield. We find that the yield measured in decay and the yield measured in steady-state emission do not, in general, coincide. We distinguish as carefully as possible the experimental situations and the material properties required for the validity of various expressions found in the literature, and we indicate the derivation of alternative expressions for models obeying nonlinear rate equations. Section VI is a summary of our results.

II. MICROSCOPIC EQUATIONS

Consider a given spatial distribution of impurities in a crystal. The Hamiltonian for impurity i, in the absence of other impurities, is denoted by $\mathcal{H}_i$. $\mathcal{H}_i$ includes all atomic effects, the effects of the crystal field, coupling to phonons, and in some circumstances, exchange terms. The $\mathcal{H}_i$ are not all necessarily the same—there may be different species or inequivalent sites. The interaction between impurities i and j is denoted as $\lambda\mathcal{H}'_{ij}$, where λ is a smallness parameter and $\mathcal{H}'_{ij}$ depends on the coordinates of both particles. The system Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}' \quad , \tag{1a}$$

where

$$\mathcal{H}_0 = \sum_i \mathcal{H}_i \quad , \tag{1b}$$

$$\mathcal{H}' = \sum_{i>j} \mathcal{H}'_{ij} \quad . \tag{1c}$$

We assume that $\mathcal{H}'$ has no terms that commute with $\mathcal{H}_0$. Although this is not entirely necessary and not always physically realistic, it simplifies the discussion.

We define our ensemble as follows: The ensemble is a set of particle distributions, each with the identical spatial configuration, but differing from each other in the states assumed by different atoms. Each member of the ensemble specifies a specific state for each individual particle. (The "individuals" within a given species are distinguished by their position. Since we are asking questions about the diffusion and migration of excitation, the position of the particles carrying the excitation can be a relevant variable. This is in contrast to the more usual situation in relaxation, where only the total number in each state is significant.) A member of the ensemble is specified by the state

$$\phi_n = \prod_i \chi_{\alpha_i}(\vec{r}_i) \quad . \tag{2}$$

The label α_i denotes the unperturbed single-particle states (with energy $E^0_{\alpha_i}$) of the particle at $\vec{r}_i$, and χ satisfies

$$\mathcal{H}_i \chi_{\alpha_i} = E^0_{\alpha_i} \chi_{\alpha_i} \quad . \tag{3}$$

If there are N_j particles of species j, and S_j states are available to each particle, then the index n can assume $\Omega = \sum_j N_j S_j$ values. In other words a change in any of the α's produces a new n. The ϕ_n are eigenstates of $\mathcal{H}_0$, corresponding to energy E^0_n, and are tremendously degenerate. Because of $\mathcal{H}'$, they are not eigenstates of $\mathcal{H}$. We denote the eigenstates of $\mathcal{H}$ by ψ_k, and they can be expanded in ϕ_n's:

$$\psi_k = \sum_{n=1}^{\Omega} c_{kn} \phi_n \quad . \tag{4}$$

The degeneracy is partially lifted by $\mathcal{H}'$. In general, a ψ_k corresponding to an energy $E_k \sim E^0_n$ will contain mainly ϕ_n's corresponding to E^0_n; conversely a given ϕ_n will, in general, be a significant component only in ψ_k's which correspond to an energy very close to E^0_n. This is not absolutely true, however, since linear combinations of ϕ_n's exist such that higher-order diagonal contributions of $\mathcal{H}'$ can become appreciable. It is also possible to have positional distributions of excitation that are long-range correlated, locally correlated, or uncorrelated. We assume that for a given energy the number of ψ_k's corresponding to correlated states is small.

Since the ψ_k are eigenstates of $\mathcal{H}$, transitions between them never occur (unless one widens the system by contact with a bath); transitions occur between the ϕ_n. At $t = 0$, we specify not an energy eigenstate ψ_k, but a state ϕ_n, which specifies *where* the excitation is. The excitation migration involves the decay of ϕ_n. The natural tool for this problem is the density matrix.

The elements of the density matrix ρ are defined in terms of the constants appearing in Eq. (4)[96]:

$$\rho_{nm} = \sum_{k=1}^{\Omega} c_{nk} c^*_{km} \tag{5a}$$

and in particular

$$\rho_{nn} = \sum_{k=1}^{\Omega} |c_{kn}|^2 \quad . \tag{5b}$$

One interprets ρ_{nn} as the probability of ϕ_n occurring in the ensemble. This is identical, by definition, to the joint probability that particle i be in state α_i, particle j in state α_j, etc.;

$$\rho_{nn} = P(\phi_n) = P[\chi_{\alpha_i}(\vec{r}_i),\ \chi_{\alpha_j}(\vec{r}_j),\ \ldots] \ . \tag{6a}$$

We will use the following shorthand, with obvious meaning:

$$\rho_n = P_n = P(i, \alpha_i; j, \alpha_j; \ \ldots) \ . \tag{6b}$$

The Pauli equation describes the time dependence of the density matrix,

$$\dot{\rho}_n = \textstyle\sum_{n'} (W_{nn'}\, \rho_{n'} - W_{n'n}\, \rho_n) \ , \tag{7}$$

where $W_{nn'}$ is the transition probability from $\phi_{n'}$ to ϕ_n. (We discuss the transition probability in more detail in Sec. IV.) The derivation of this equation has been intensely studied, the central problem being the progressive removal of conditions that are sufficient but not necessary.[97] The equation applies, in general, to weakly coupled dilute systems (but it is possible to derive more general equations). By "weakly coupled" one means that the states ϕ_n, and therefore χ_α, remain suitable basis states for all time; by "dilute" one means that multiparticle collisions or interactions do not dominate the relaxation process. More precisely the following constraints apply: (i) The N/V limit holds, i.e., the effects are concentration dependent, but not volume dependent. (ii) In Eq. (1a) the smallness parameter λ goes to zero as the time t goes to infinity, but $\lambda^2 t$ is finite. This condition guarantees that the perturbation remains small even when applied for a long period of time. It implies that the autocorrelation time of $\mathcal{H}'$ is short compared with the time scale of measurement. It excludes, in particular, strong-coupling cases, as may in practice be sometimes encountered with exchange. Such cases must be handled separately, usually by redefining the "particles" in such a way that the coupling terms are already included in $\mathcal{H}_0$. A derivation which particularly elucidates this constraint is given by Montroll.[98] (iii) The off-diagonal elements of ρ are initially zero, i.e., the random-phase approximation is valid at $t=0$. This constraint excludes effects which depend on the order or coherence of the system, as may be encountered, for instance, with phase-locked laser-driven systems.

We observe that with the interpretation of ρ given by Eq. (6), the Pauli equation (7) is identical to the master equation of Falkoff.[99,100]

The final states $\phi_{n'}$ can be classified with respect to ϕ_n according to the number of particles that have changed state. We focus our initial attention to binary processes. This is notationally convenient, and the generalization to higher-order processes is easy. We consider one particular binary term, in which atom i deexcites and atom j excites:

$$\begin{aligned}(\dot{\rho}_n)_{ij} = \sum_{\bar{\alpha}_i}{}' \sum_{\bar{\alpha}_j}{}' \; & W(\vec{r}_i, \vec{r}_j, \bar{\alpha}_i, \bar{\alpha}_j, \alpha_i, \alpha_j)\, P(1, \alpha_1; \cdots i, \bar{\alpha}_i; \cdots j, \bar{\alpha}_j; \cdots N, \alpha_N) \\ & - W(\vec{r}_i, \vec{r}_j, \alpha_i, \alpha_j, \bar{\alpha}_i, \bar{\alpha}_j)\, P(1, \alpha_1; \cdots i, \alpha_i; \cdots j, \alpha_j; \cdots N, \alpha_N) \ . \end{aligned} \tag{8}$$

Here, the labels α denote the initial particle states, as specified by ϕ_n and the $\bar{\alpha}$ denote the changed final particle states, as specified by $\phi_{n'}$. For binary processes, only two of the final particle states differ from the initial ones. The prime on the sum over final states indicates that the initial states are to be omitted from the sum. In general, W will depend on the initial and final particle states and on the relative positions of the particles. In particular it will be zero for transitions which do not conserve energy. The time dependence of ρ due to all possible binary processes is given by

$$\dot{\rho}_n = \frac{1}{2} \sum_{i \neq j} \sum (\dot{\rho}_n)_{ij} \ , \tag{9}$$

where $(\dot{\rho}_n)_{ij}$ is defined in Eq. (8). We note that

$$\frac{1}{2} \sum_{i \neq j} \sum = \sum_{i > j} \sum \ .$$

We now transform Eq. (9) which deals with states of the N-body system to an equation which deals with individual particle states. The probability of finding particle k in a particular state, which we denote by α_k, is given by

$$P(k, \alpha_k) = \textstyle\sum_n' \rho_n \tag{10}$$

and its time dependence by

$$\dot{P}(k, \alpha_k) = \textstyle\sum_n' \dot{\rho}_n \ , \tag{11}$$

where the primed sum includes all n such that ϕ_n contains $\chi_{\alpha_k}(\vec{r}_k)$. To perform the sum in Eq. (11) we sum Eq. (8) over all initial states, with fixed α_k:

$$\begin{aligned}\dot{P}(k, \alpha_k) = \frac{1}{2} \sum_{i \neq j} \sum \sum_{\bar{\alpha}_i}{}' \sum_{\bar{\alpha}_j}{}' \prod_{n \neq k} \sum_{\alpha_n} \; & [W(\vec{r}_i, \vec{r}_j, \bar{\alpha}_i, \bar{\alpha}_j, \alpha_i, \alpha_j)\, P(1, \alpha_1; \cdots i, \bar{\alpha}_i; \cdots j, \bar{\alpha}_j; \cdots N, \alpha_N) \\ & - W(\vec{r}_i, \vec{r}_j, \alpha_i, \alpha_j, \bar{\alpha}_i, \bar{\alpha}_j)\, P(1, \alpha_1; \cdots i, \alpha_i; \cdots j, \alpha_j; \cdots N, \alpha_N)] \ . \end{aligned} \tag{12}$$

Here we indicate by the symbol $\Pi_{n\neq k}\sum_{\alpha_n}$ that one sums over all the initial states of all particles except the kth. These sums allow us to contract Eq. (12) by means of the summation theorem for joint probabilities,[99] $\sum_m P(m,n)=P(n)$, where both m and n may denote sets of variables.

Consider the sums over states for fixed i and j. There are two cases: (a) Neither i nor j equals k. (b) Either i or j equals k. In case (a), k does not change its state α_k. We would expect the contributions from such terms to sum to zero, and we now demonstrate that this is indeed so. Using the summation theorem to sum the right-hand side of Eq. (12) over all states except the initial and final states of i, j, and k, we obtain, for fixed i and j,

$$\frac{1}{2}\sum_{\bar\alpha_i}{}'\sum_{\bar\alpha_j}{}'\sum_{\alpha_i}\sum_{\alpha_j} W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_j,\bar\alpha_i,\bar\alpha_j,\alpha_i,\alpha_j)P(i,\bar\alpha_i;j,\bar\alpha_j;k,\alpha_k)-W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_j,\alpha_i,\alpha_j,\bar\alpha_i,\bar\alpha_j)P(i,\alpha_i;j,\alpha_j;k,\alpha_k)\ .$$

Since α_i and $\bar\alpha_i$ run over the same set of states, as do α_j and $\bar\alpha_j$, the summation cancels the terms identically. On the other hand, if i equals k, the summation over all but $\bar\alpha_i$, α_i, and $\bar\alpha_k$ gives

$$\frac{1}{2}\sum_{\bar\alpha_i}{}'\sum_{\bar\alpha_k}{}'\sum_{\alpha_i} W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_k,\bar\alpha_i,\bar\alpha_k,\alpha_i,\alpha_k)P(i,\bar\alpha_i;k,\bar\alpha_k)-W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_k,\alpha_i,\alpha_k,\bar\alpha_i,\bar\alpha_k)P(i,\alpha_i;k,\alpha_K)\ .$$

Because α_k is exempt from summation, these terms do not cancel. If j equals k, a similar expression results, with the dummy index j substituted for the dummy index i. The double sum over i and j is therefore reduced to a single sum, and Eq. (12) becomes

$$\dot P(k,\alpha_k)=\sum_i\sum_{\bar\alpha_i}{}'\sum_{\alpha_i}\sum_{\bar\alpha_k} W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_k,\bar\alpha_i,\bar\alpha_k,\alpha_i,\alpha_k)P(i,\bar\alpha_i;k,\bar\alpha_k)-W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_k,\alpha_i,\alpha_k,\bar\alpha_i,\bar\alpha_k)P(i,\alpha_i;k,\alpha_k)\ . \tag{13}$$

It should be noted that energy conservation enters only through W, which must vanish if energy is not conserved. If one is talking about a pair of levels α_k and $\bar\alpha_k$ in resonance with another pair α_i and $\bar\alpha_i$, then only one term in the triple sum of Eq. (13) will have a nonvanishing coefficient.

If no "bath" variables are implicitly integrated over in W, then the W's for a process and its inverse are equal. This condition is verified for resonant transfers (although it is not verified for phonon-assisted transfers). To reduce notation, we shall henceforth write W only once.

To facilitate progress, it is convenient to factor the joint probability distributions of Eq. (13). The assumption of factorizability means that correlations among the populations of single-particle states remain infinitesimal for all time; i.e., there are no fluctuations into coherent many-body states. For further discussion of this point we refer to Ref. 99. At first sight, this seems to go beyond condition (3) for the Pauli equation, which requires lack of coherence at $t=0$. However, Kac[101] has proved that if the off-diagonal elements of the density matrix vanish at $t=0$, then they remain zero for all time, for isolated systems. Factorizability does not impose a constraint over and above what is already required by the Pauli equation. This fact would be difficult to establish without the identification we have made between a spatial distribution and the density matrix. In factored form, Eq. (13) reads

$$\dot P(k,\alpha_k)=\sum_i\sum_{\bar\alpha_i}{}'\sum_{\alpha_i}\sum_{\bar\alpha_k}{}' W(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_k,\bar\alpha_i,\bar\alpha_k,\alpha_i,\alpha_k)\times[P(i,\bar\alpha_i)P(k,\bar\alpha_k)-P(i,\alpha_i)P(k,\alpha_K)]\ . \tag{14}$$

We make two additional remarks:

(a) If there are two species, it is convenient to group the terms in Eq. (14) with explicit reference to the two species. We use A and B as subscripts to denote each species, and we label the states available to an A particle as α, and those available to a B particle as β. Then Eq. (14) becomes

$$\begin{aligned}\dot P_A(k,\alpha_k)=&\sum_j\sum_{\bar\beta_j}{}'\sum_{\beta_j}\sum_{\bar\alpha_k}{}' W_{AB}(\vec{\mathrm{r}}_j,\vec{\mathrm{r}}_k,\bar\beta_j,\bar\alpha_k,\beta_j,\alpha_k)[P_A(k,\bar\alpha_k)P_B(j,\bar\beta_j)-P_A(k,\alpha_k)P_B(j,\beta_j)]\\&+\sum_i\sum_{\bar\alpha_i}{}'\sum_{\alpha_i}\sum_{\bar\alpha_k}{}' W_{AA}(\vec{\mathrm{r}}_i,\vec{\mathrm{r}}_k,\bar\alpha_i,\bar\alpha_k,\alpha_i,\alpha_k)[P_A(i,\bar\alpha_i)P_A(k,\bar\alpha_k)-P_A(i,\alpha_i)P_A(k,\alpha_k)]\ .\end{aligned} \tag{15}$$

The first sum accounts for intersystem (A-B) transfers. The second sum accounts for intrasystem (A-A) transfers.

(b) If W permits interactions not between two but between Q particles, it is clear that the corresponding terms on the right-hand side of Eq. (14) will be

$$\left(\sum_i \sum_{\bar{\alpha}_i}{}' \sum_{\alpha_i}\right)\left(\sum_j \sum_{\bar{\alpha}_j}{}' \sum_{\alpha_j}\right)\cdots \sum_{\bar{\alpha}_k}{}' W(\vec{r}_i, \vec{r}_j, \ldots \vec{r}_k, \bar{\alpha}_i, \bar{\alpha}_j, \ldots \bar{\alpha}_k, \alpha_i, \alpha_j, \ldots \alpha_k)$$

$$\times[P(i, \bar{\alpha}_i)P(j, \bar{\alpha}_j)\cdots P(k, \bar{\alpha}_k) - P(i, \alpha_i)P(j, \alpha_j)\cdots P(k, \alpha_k)] \; , \qquad (16)$$

where the notation $\cdots$ indicates a total of $(Q-1)$ similar factors or variables, not counting k.

Of course, the equations we have derived are only typical of a set, in the sense that a similar equation can be derived for each state available to each species.

The equations we have so far derived deal with one fixed spatial configuration of particles. This model is realistic in the sense that particles, of course, do occupy some fixed configuration; it is unrealistic in the sense that this configuration is unknown and that, more important, the macroscopic properties cannot depend on it. In particular, sums over particles which appear in calculations are invariably replaced by sums over lattice sites. Therefore, it is desirable to derive at the outset the time development of a probability whose variables include coordinates. Such a probability is the joint probability that there is a particle at $\vec{r}_a$ and that it is in state α_k, denoted $P(\vec{r}_a, \alpha_k)$—as opposed to the simple probability that the particle fixed at $\vec{r}_k$ is in state α_k which we have denoted $P(k, \alpha_k)$. The derivation merely requires that we enlarge our ensemble. That is, Eq. (2) is now modified to

$$\phi_n = \prod_i \chi_{\alpha_i}(\vec{r}_a^{\,i}) \; , \qquad (2')$$

where the superscript on $\vec{r}$ refers to the particle and the subscript to its lattice site. Since we now distinguish between a particle and its position, we define, in addition to $P(k, \alpha_k)$ and $P(\vec{r}_a, \alpha_k)$, the function $P(\vec{r}_a, k, \alpha_k)$ as the probability that the particle k is located at $\vec{r}_a$ and that its state is α_k.

We note the following relations:

$$\textstyle\sum_{r_a} P(\vec{r}_a, k, \alpha_k) = P(k, \alpha_k) \; , \qquad (17a)$$

$$\textstyle\sum_k P(\vec{r}_a, k, \alpha_k) = P(\vec{r}_a, \alpha_k) \; , \qquad (17b)$$

$$\textstyle\sum_{\alpha_k} P(\vec{r}_a, k, \alpha_k) = P(\vec{r}_a, k) \; , \qquad (17c)$$

$$\textstyle\sum_{r_a} P(\vec{r}_a, \alpha_k) = \sum_k P(k, \alpha_k) = N_{\alpha_k} \; , \qquad (17d)$$

$$\textstyle\sum_{r_a} P(\vec{r}_a, k) = 1 \; . \qquad (17e)$$

The joint probability corresponding to ρ_n is accordingly

$$\rho_n = P_n = P(\vec{r}_a, i, \alpha_i; \vec{r}_b, j, \alpha_j; \ldots) \; . \qquad (6b')$$

There are no transitions between configurations. Therefore Eq. (8) remains intact, except that the joint probabilities are given by Eq. (6b$'$) and the right-hand side is preceded by a sum over configurations. We note that the sum over configurations is equivalent to

$$\sum_c = \sum_{\vec{r}_l^{\,1}}{}' \sum_{\vec{r}_m^{\,2}}{}' \cdots \sum_{\vec{r}_p^{\,k-1}}{}' \sum_{\vec{r}_q^{\,k+1}}{}' \cdots \sum_{\vec{r}_z^{\,N}}{}' \; ,$$

where $\sum_{\vec{r}_n^{\,j}}'$ means that the position $\vec{r}_n^{\,j}$ of particle j assumes successively the values 1 to M, where M is the number of lattice sites, excepting only the values of $\vec{r}$ occupied by the particles k and i. Equations (10)–(12) now refer to $P(\vec{r}_a, k, \alpha_k)$ rather than $P(k, \alpha_k)$, and of course have $\sum_c$ preceding their right-hand sides. All the arguments go through essentially unchanged, and Eqs. (17) allow the contraction into $P(\vec{r}_a, \alpha_k)$ rather than $P(k, \alpha_k)$. The final result, paralleling Eq. (14), is

$$\dot{P}(\vec{r}_a, \alpha_k) = \sum_{\vec{r}_b} \sum_{\bar{\alpha}_i}{}' \sum_{\alpha_i} \sum_{\bar{\alpha}_k}{}' W(\vec{r}_b, \vec{r}_a, \bar{\alpha}_i, \bar{\alpha}_k, \alpha_i, \alpha_k)[P(\vec{r}_b, \bar{\alpha}_i)P(\vec{r}_a, \bar{\alpha}_k) - P(\vec{r}_b, \alpha_i)P(\vec{r}_a, \alpha_k)] \; , \qquad (14')$$

and paralleling Eq. (15),

$$\dot{P}_A(\vec{r}_a, \alpha_k) = \sum_{\vec{r}_b} \sum_{\bar{\beta}_j}{}' \sum_{\beta_j} \sum_{\alpha_k}{}' W_{AB}(\vec{r}_b, \vec{r}_a, \bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k)[P_A(\vec{r}_a, \bar{\alpha}_k)P_B(\vec{r}_b, \bar{\beta}_j) - P_A(\vec{r}_a, \alpha_k)P_B(\vec{r}_b, \beta_j)]$$

$$+ \sum_{\vec{r}_b} \sum_{\bar{\alpha}_i}{}' \sum_{\alpha_i} \sum_{\bar{\alpha}_k}{}' W_{AA}(\vec{r}_b, \vec{r}_a, \bar{\alpha}_i, \bar{\alpha}_k, \alpha_i, \alpha_k)[P_A(\vec{r}_a, \bar{\alpha}_k)P_A(\vec{r}_b, \bar{\alpha}_i) - P_A(\vec{r}_a, \alpha_k)P_A(\vec{r}_b, \alpha_i)] \; . \qquad (15')$$

In Eqs. (14$'$) and (15$'$) we have produced, in the strictest sense, equations for a microscopic density function.

The procedure leading to Eq. (15$'$) is equivalent to taking a configuration average of Eq. (15). The configuration average of an operator $O(\vec{r}_1, \ldots, \vec{r}_N)$

is defined as the following integral over volume V, or sum over M lattice sites:

$$\langle O\rangle_c = \frac{1}{V^N}\int O(\vec{r}_1, \cdots, \vec{r}_N)\,d\vec{r}_1\cdots d\vec{r}_N \tag{18a}$$

$$= \frac{1}{M^N}\sum_{\vec{r}_1}\cdots\sum_{\vec{r}_N} O(\vec{r}_1, \ldots, \vec{r}_N)\ . \tag{18b}$$

The difficulty with the configuration average, as given, is that it does not exclude configurations in which more than one particle occupies the same site. One can easily exclude more than one particle from the specific sites under consideration [e.g., a and b in Eq. (14′)]. But the excluded volume problem in general is unsolved. It is disconcerting to realize that the fraction of allowed configurations is exponentially infinitesimal. There is a counter-consideration, however: From the Ursell-Mayer[102] linked-cluster theory for the imperfect gas it is known that the configuration average is valid in the limit of vanishing concentrations. At worst, therefore, one is calculating properties of the interacting system to an accuracy corresponding to the first virial coefficient. The convergence of the linked-cluster expansion hinges on the finite range of certain functions f_{ij}. It is easily shown that in the present context the corresponding functions are δ functions, except for a finite number which can be handled separately. (The problem is therefore reduced from integration to counting.) For this reason we hypothesize that the configuration average is valid in the present context even for finite concentrations.

We remark that the simplicity of our derivation hinges on the choice of ensemble, which is an ensemble in "Γ" space rather than in "μ" space.[96] The Pauli equation is thus linear with respect to the system states, but highly nonlinear with respect to single-particle states; in the transformation the dimensionality of its space has been tremendously reduced.

We have packed exchange and phonons into $\mathcal{H}_i$, although in principle such interactions could be explicitly treated. With reference to transfer, phonons have four effects: (i) They cause line shifts, including Stokes shift, which alter the resonant condition. (ii) They cause (inhomogeneous) line broadening, which imposes a statistical treatment on the resonance condition. These effects are significant for transition metals but not in general for rare earths. (iii) They cause electron-lattice relaxation, producing terms linear in single-particle probabilities, which are easily included. (iv) They produce a second-order effective interparticle interaction, which we have discussed previously.[26] We shall not develop here any of these effects explicitly.

III. MACROSCOPIC EQUATIONS

To solve the equations for the density function, in general, is difficult, because of their nonlinear and nonlocal character. It is possible to devise iterative procedures, and to limit artificially the range of nonlocality. Rather than pursue this direction, however, we shall restrict ourselves to limiting cases which yield expressions actually current in the literature.

In Eqs. (15) and (15′) there are two sums—the (AB) term which represents intersystem transfer, and the (AA) term which represents intrasystem transfer. We consider cases where the magnitudes of (AB) and of (AA) are sufficiently different so that one can define three time scales: t_{AB}, t_{AA}, and t_m, the time scale of measurement. The condition $t_{AA}\ll t_m\ll t_{AB}$ corresponds to the assumption that internal thermalization within the A system is much more rapid than A-B transfer. Under this assumption we shall derive the usual kinetic nonlinear rate equations. The condition $t_m\ll t_{AB}\ll t_{AA}$ corresponds to the assumption that A-B transfer is much more rapid than internal thermalization of system A (or system B). After a number of additional constraints, we shall derive the decay equations used by Forster,[2–6] Colbow,[16,18] and Inokuti and Hirayama.[17]

We now consider the limit $t_{AA}\ll t_m\ll t_{AB}$. In Eq. (15) or (15′), as the (AA) term becomes very large, one can neglect the (AB) term. In this limit, the steady state is reached, or the (AA) term becomes vanishing, in a time shorter than any other relevant time. The structure of the (AA) term is such that the steady state requires $P(i,\alpha_k)=P(k,\alpha_k)$, or $P(\vec{r}_i,\alpha_k)=P(\vec{r}_k,\alpha_k)$, for every i, k, and α_k. Physically, this means the A system follows any A-B transfer adiabatically, and the distribution of the various states α is spatially homogeneous, on the time scale t_m.

We now address ourselves specifically to Eq. (15′). We sum Eq. (15′) on $\vec{r}_a$. The (AA) term vanishes identically upon summation, and, using (17d), we obtain

$$\dot{N}_{\alpha_k} = \sum_{\bar{\beta}_j}{}'\sum_{\beta_j}\sum_{\bar{\alpha}_k}{}'\sum_{\vec{r}_a}\sum_{\vec{r}_b} W_{AB}(\vec{r}_b, \vec{r}_a, \bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k) \times[P_A(\vec{r}_a,\bar{\alpha}_k)P_B(\vec{r}_b,\bar{\beta}_j) - P_A(\vec{r}_a,\alpha_k)P_B(\vec{r}_b,\beta_j)]\ . \tag{19}$$

Since $P_A(\vec{r}_a,\bar{\alpha}_k)$ and $P_A(\vec{r}_a,\alpha_k)$ are independent of $\vec{r}_a$, they can be pulled out of the $\vec{r}_a$ and $\vec{r}_b$ sums. Their actual value is

$$P_A(\vec{r}_a,\bar{\alpha}_k) = P_A(\bar{\alpha}_k) \equiv n_{\bar{\alpha}k}\ , \tag{20a}$$

$$P_A(\vec{r}_a,\alpha_k) = P_A(\alpha_k) \equiv n_{\alpha k}\ , \tag{20b}$$

where n is a molar concentration (i.e., N/M; M is the number of sites). We assume at this point that W depends on $\vec{r}_b$ and $\vec{r}_a$ only through their difference $(\vec{r}_a - \vec{r}_b)$, an assumption which is physically justified in nearly all circumstances. We define

$$\langle W(\bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k)\rangle = \textstyle\sum_{\vec{r}_a} W(\vec{r}_a - \vec{r}_b, \bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k)\,, \tag{21}$$

and we note that in virtue of our assumption, the sum in Eq. (21) is independent of origin, that is of the value of $\vec{r}_b$. Using Eqs. (20), (21), and (17d), Eq. (19) becomes

$$\dot{n}_{\alpha_k} = \textstyle\sum'_{\bar{\beta}_j} \sum_{\beta_j} \sum'_{\bar{\alpha}_k} \langle W_{AB}(\bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k)\rangle \times [n_{\bar{\alpha}_k} n_{\bar{\beta}_j} - n_{\alpha_k} n_{\beta_j}]\,. \tag{22}$$

This is the familiar form of the nonlinear rate equation for binary processes. Frequently there are only two pairs of interacting levels in resonance, and then the sums over states would collapse to one term.

We have chosen to derive Eq. (22) from Eq. (15′), which is the configuration-averaged version of Eq. (15). To see what price is paid if we wish to avoid the configuration average, we now derive Eq. (22) directly from Eq. (15). Equation (15) is summed on k. Similar considerations as before apply to the P_A's except that their constant value is now n_α/n_A rather than n_α. What is different is that we must now consider $\sum_k W(\vec{r}_k, \vec{r}_j, \bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k)$ which is a sum over particles, not over sites. To make this sum invariant with respect to the origin $\vec{r}_j$, we must assume that each particle sees an identical configuration of particles, with respect to its own origin. This means that the spatial distribution is not random but forms a lattice. To convert the sum further into a lattice sum over all points, i.e., to put

$$\begin{aligned}\textstyle\sum_k W(\vec{r}_k - \vec{r}_j, \bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k) &= \textstyle\sum_{\vec{r}_a} n_A W(\vec{r}_a - \vec{r}_b, \bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k) \\ &= n_A \langle W(\bar{\beta}_j, \bar{\alpha}_k, \beta_j, \alpha_k)\rangle\,,\end{aligned} \tag{23}$$

we must assume in addition that every lattice site is occupied by n_{α_1} particles in state α_1, by n_{α_2} particles in state α_2, and so on for every state α_k. With Eq. (23), one moves in straightforward fashion from Eqs. (15)–(22). Equation (23), or essentially similar ones, are very common in the literature. We feel that the implied physical model is difficult to sustain, and we prefer the configuration average, with its own difficulties. In the present context, the results turn out the same, but this is not always the case.

We make three further remarks: (a) The rate equation (22), which we have derived, is usefully written in terms of the fractional occupation numbers

$$p_\alpha = n_\alpha / n_A\,, \tag{24a}$$

$$q_A = n_\alpha / n_{\text{total}}\,. \tag{24b}$$

Abbreviating the notation to show only two pairs of states, Eq. (22) then becomes

$$\dot{p}_\alpha = \langle W\rangle n_B (p_{\bar{\alpha}} p_{\bar{\beta}} - p_\alpha p_\beta)\,, \tag{25a}$$

$$\dot{q}_\alpha = \langle W\rangle n_T (q_{\bar{\alpha}} a_{\bar{\beta}} - q_\alpha q_\beta)\,. \tag{25b}$$

The notation (25b) produces systems of equations whose symmetry in α and β is more apparent. (b) The sum over sites which defines $\langle W\rangle$ is conveniently replaced by an integral whose lower limit is the distance to an effective nearest-neighbor lattice site. This distance may be the true nearest-neighbor distance, the radius of a sphere whose volume equals the volume of a unit cell, or a similar geometrical dimension. The error incurred is usually, though not always, small. For a more complete discussion of this point, we refer to a previous paper by the author.[103] (c) Our derivation of the rate equation has not involved any assumption about t_{BB}. Likewise, had we assumed t_{BB} to be short, then without further assumption about t_{AA} we could have derived an equation for n_β. Since the time dependences of n_α and n_β are rigidly coupled by energy and particle conservation, it follows that rapid thermalization of either species, not necessarily both, is sufficient for the appropriateness of the rate equations.

We now consider the limit $t_m \ll t_{AB} \ll t_{AA}$. In Eqs. (15) and (15′) the (AA) terms can now be neglected. In Eq. (15′), $P_A(\vec{r}_a, \alpha)$ is now not constant, however, and varies randomly with $\vec{r}_a$. To disentangle the time dependence from this random coordinate dependence is difficult. But Eq. (15), in which only particle labels appear, can be solved under this approximation.

We define

$$\Delta_{l\gamma}(t) = P(l, \gamma_l) - P(l, \gamma_l)_\infty\,, \tag{26}$$

where the subscript indicates the equilibrium value, attained as $t \to \infty$. Neglecting terms higher than linear in Δ's (and neglecting the possibility of multiple resonances), Eq. (15) now becomes

$$\dot{\Delta}_{k\alpha} = \textstyle\sum_j W(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)[\Delta_{j\bar{\beta}} P(k, \bar{\alpha})_\infty + \Delta_{k\bar{\alpha}} P(j, \bar{\beta})_\infty - \Delta_{j\beta} P(k, \alpha)_\infty - \Delta_{k\alpha} P(j, \beta)_\infty]\,. \tag{27}$$

This linearization of Eq. (15) will be a valid approximation provided (i) the displacements from equilibrium Δ are small for all time, and (ii) the particle concentrations are low. The second condition arises in physically more comprehensive equations from the requirement that the quadratic terms must be negligible also with respect to linear dissipation terms which will in general appear.

A number of alternative additional simplifications are now required:

Case 1. (a) $P(k,\alpha)_\infty \simeq 0$, i.e., the initially excited state (of the sensitizer) will be fully depleted; (b) $P(j,\beta)_\infty \simeq 1$, i.e., the initially fully populated ground state (of the activator) will not be significantly depleted; and (c) the backflow terms are negligible.

Constraints (a) and (b) are in conflict, unless the initial fractional occupation of the excited state is very small. Constraint (c) implies physically that the sensitizer have a concentration much lower than the activator, and that t_{BB} as well as t_{AA} be long. These conditions are in addition to the ones required for linearization. They allow the neglect of all but the last term on the right-hand side of Eq. (27), which then reduces to

$$\dot{\Delta}_{k\alpha} = -\textstyle\sum_j' W_{AB}(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)\, \Delta_{k\alpha} \ , \qquad (28)$$

with solution

$$\Delta_{k\alpha} = \exp[-\textstyle\sum_j W_{AB}(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)\, t] \ . \qquad (29)$$

Alternatively, in a process such as ionized donor-acceptor recombination luminescence, the particles deexcite in pairs. This is case 2.

Case 2. This requires (a) $P(j,\bar{\beta})_\infty = P(k,\bar{\alpha})_\infty = 1$, (b) $P(j,\beta)_\infty = P(j,\alpha)_\infty = 0$. With these constraints, Eq. (27) reduces to

$$\dot{\Delta}_{k\alpha} = -2\textstyle\sum_j W_{AB}(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)\, \Delta_{k\alpha} \ , \qquad (30)$$

with solution

$$\Delta_{k\alpha} = \exp[-2\textstyle\sum_j W_{AB}(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)\, t] \ . \qquad (31)$$

It is at this point that we perform the configuration average, in order to handle the sums over particles in a random distribution. We then obtain, for cases 1 and 2, respectively,

$$\langle \Delta\alpha \rangle = \frac{1}{V^N} \int \exp[-W_{AB}(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)\, t] \times d\vec{r}_1 \cdots d\vec{r}_N \ , \qquad (32a)$$

$$\langle \Delta\alpha \rangle = \frac{1}{V^N} \int \exp[-2W_{AB}(\vec{r}_k, \vec{r}_j, \bar{\alpha}, \bar{\beta}, \alpha, \beta)\, t] \times d\vec{r}_1 \cdots d\vec{r}_N \ . \qquad (32b)$$

We point out that there is no conflict between the nonexponential time dependence of Eq. (32) and the linearized equation (27) from which it is derived. The decay is the sum of N exponentials, and indeed is equivalent to summing Eq. (29) or (31) on k. Our inability to perform directly either this sum or the sum in the exponent is, of course, what motivates the configuration average. It is interesting to note that the prescription (23) would lead to a simple exponential in this case, in contrast to the result of the configuration average.

Equations (32) are the starting equations of Forster in his series of papers beginning in 1948. They were applied specifically to exchange by Colbow in 1965, and a number of generalizations were subsequently made by Inokuti and Hirayama in 1965. We shall refer to models in which the assumptions underlying Eqs. (32) are verified as FCIH models. It should be pointed out, however, that equations of the form of Eq. (32) have a long history outside the field of luminescence, and have been used to solve problems as various as pressure broadening in gasses,[104,105] calculations of equations of state,[102] and the calculation of paramagnetic resonance line shapes.[103,106–108]

We have exhibited with some care, and in sequence, the assumptions underlying Eqs. (32). It is apparent that they apply more naturally to case 2, the context of the Colbow calculation, for instance, than they do to case 1 or to transfer properly speaking. There are important physical systems to which the numerous restrictions are undoubtedly applicable—in the context, for instance, of fluorescent dyes, for which the theory was proposed by Forster. Their applicability to conditions encountered in many inorganic systems must be scrutinized carefully, however. In the context of rare-earth impurities in crystals, for instance, it seems that the concentration ranges encountered, the levels of excitation that are achieved, and the relative magnitudes of the various transfer times all render this model inappropriate. We shall return to this point later.

IV. TRANSITION PROBABILITIES

In this section we discuss (a) the first-order transition probabilities, (b) multiparticle transition probabilities, (c) the effects of certain generalizations in $\mathcal{H}'$, and (d) the concentration dependence of $\langle W \rangle$.

(a) The first-order transition probability is given by the usual expression

$$W(\vec{r}_j, \vec{r}_k, \bar{\alpha}, \bar{\beta}, \alpha, \beta) = (2\pi/\hbar) |\mathcal{H}'_{nn'}|^2 \rho(E) \ . \qquad (33)$$

The initial and final states correspond to ϕ_n and $\phi_{n'}$, defined in Eq. (2). If $\mathcal{H}'$ contains only two-particle operators, i.e., if $\mathcal{H}'$ obeys Eq. (1c), then the transition matrix element written in full is

$$\mathcal{H}'_{nn'} = \langle \chi_{\bar{\alpha}}(\vec{r}_k), \chi_{\bar{\beta}}(\vec{r}_j) | \tfrac{1}{2}\mathcal{H}'(\vec{r}_j, \vec{r}_k) | \chi_\alpha(\vec{r}_k), \chi_\beta(\vec{r}_j) \rangle \ . \qquad (34)$$

The density of states $\rho(E)$ is simply 1 or 0, depending on whether or not $(E_\alpha - E_{\bar{\alpha}}) + (E_\beta - E_{\bar{\beta}}) = 0$. This is true only if $\mathcal{H}'$ has no diagonal elements and is time independent. Relaxation of these conditions on $\mathcal{H}'$ is discussed under (c).

(b) The transition probabilities for processes involving more than two particles require higher-order matrix elements (if $\mathcal{H}'$ contains only two particle terms). These can readily be obtained from standard perturbation theory.[109] Such multiparticle processes are well known in paramagnetic relaxation, for instance.[110–112] We exhibit the matrix element for three particles which change from states α, β, γ to states $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}$. We abbreviate the notation to indicate only states, not coordinates, and we indicate intermediate states by the subscript "m":

$$\begin{aligned}\mathcal{H}_{n'n}=&\sum_{\beta_m}\frac{\langle\bar{\gamma}\bar{\beta}\,|\mathcal{H}'|\,\gamma\beta_m\rangle\langle\beta_m\bar{\alpha}\,|\mathcal{H}'|\,\beta\alpha\rangle}{E_\alpha-E_{\bar{\alpha}}+E_\beta-E_{\beta_m}}+\sum_{\alpha_m}\frac{\langle\bar{\gamma}\bar{\alpha}\,|\mathcal{H}'|\,\gamma\alpha_m\rangle\langle\alpha_m\bar{\beta}\,|\mathcal{H}'|\,\alpha\beta\rangle}{E_\alpha-E_{\alpha_m}+E_\beta-E_{\bar{\beta}}}\\&+\sum_{\gamma_m}\frac{\langle\bar{\beta}\bar{\gamma}\,|\mathcal{H}'|\,\beta\gamma_m\rangle\langle\gamma_m\bar{\alpha}\,|\mathcal{H}'|\,\gamma\alpha\rangle}{E_\alpha-E_{\bar{\alpha}}+E_\gamma-E_{\gamma_m}}+\sum_{\alpha_m}\frac{\langle\bar{\beta}\bar{\alpha}\,|\mathcal{H}'|\,\beta\alpha_m\rangle\langle\alpha_m\bar{\gamma}\,|\mathcal{H}'|\,\alpha\gamma\rangle}{E_\alpha-E_{\alpha_m}+E_\gamma-E_{\bar{\gamma}}}\\&+\sum_{\beta_m}\frac{\langle\bar{\alpha}\bar{\beta}\,|\mathcal{H}'|\,\alpha\beta_m\rangle\langle\beta_m\bar{\gamma}\,|\mathcal{H}'|\,\beta\gamma\rangle}{E_\beta-E_{\beta_m}+E_\gamma-E_{\bar{\gamma}}}+\sum_{\gamma_m}\frac{\langle\bar{\alpha}\bar{\gamma}\,|\mathcal{H}'|\,\alpha\gamma_m\rangle\langle\gamma_m\bar{\beta}\,|\mathcal{H}'|\,\gamma\beta\rangle}{E_\beta-E_{\bar{\beta}}+E_\gamma-E_{\bar{\gamma}}}\ .\end{aligned}\tag{35}$$

For Q particles ($Q>2$), there will be $Q!$ sums, each on $(Q-2)$ indices. It is, of course, the square of the absolute value of such expressions that enters the transition probability. Interference does not, in general, occur, and the cross terms remain. Despite this plethora of terms, the multiparticle interactions are limited by the large energy denominators, and the "weak-coupling" requirement of the Pauli equation guarantees precisely that such an expansion will not diverge.

It may happen, however, that a particular multiparticle process happens with high probability. This occurs when a Q-particle process is forbidden because of a near miss in resonance or because of a vanishing matrix element, but a related $(Q+1)$ particle process is allowed. Consider, for example, the system of levels shown in Fig. 1. Suppose the two-particle process $5\rightarrow4$, $0\rightarrow4$ is inhibited, either because one of the matrix elements vanishes, or because $(E_5-E_4)>(E_4-E_0)$. Suppose that the three-particle process $5\rightarrow1$, $0\rightarrow4$, $0\rightarrow4$ is not inhibited by selection rules, however, and conserves energy. In Eq. (35) there will occur energy denominators like $(E_5+E_0-2E_4)$ which are small, and which give rise to a large probability for this process. The missed or forbidden resonance for the two-particle process thus actually appears in an associated three-particle process. This will be the rule rather than the exception whenever a closely spaced subset of levels is available which can provide intermediate Q-particle states which differ only narrowly in energy from the initial state. This consideration is important in applications.

(c) We now consider modifications that arise when $\mathcal{H}'$ (i) has diagonal elements and (ii) is time dependent. In general, $\mathcal{H}'$ will have parts that commute with $\mathcal{H}_0$. This is likely to be true even if $\mathcal{H}_0$ and $\mathcal{H}'$ are basically of different symmetry, since both states and interactions are rarely pure symmetry types. Likewise, in general, $\mathcal{H}'$ fluctuates, often in a random way. The neglect of these fluctuations is justified if the energy associated with them is negligible. These are vast subjects, and well known in the theory of relaxation.[113,114] We summarize the principal relevant results. It is usual to redefine $\mathcal{H}_0$ so as to include all diagonal contributions. Correlatively this redefines the single-particle states of Eq. (3) and therefore the states ϕ_n of the system. Factorization into the states χ_α defined by Eq. (3) is no longer possible, since the particle states themselves now contain interaction terms. For weakly interacting systems one can usefully define quasiparticles, with energy levels similar to those of the bare particles, except that they have a concentration-dependent width. The time dependence of $\mathcal{H}'$ not merely modulates $\mathcal{H}'$ but has an energy of its own associated with it, which depends on the frequencies present in it. Both this energy and the level width operate to relax energy conservation, to the extent that the interactions can supply the balance. (As a rule of thumb, this corresponds to the nearest-neighbor interaction energy.) Both factors again operate to make the density of states that enters the transition probability concentration dependent, in a complicated fashion. [Again as a rule of thumb, for ex-

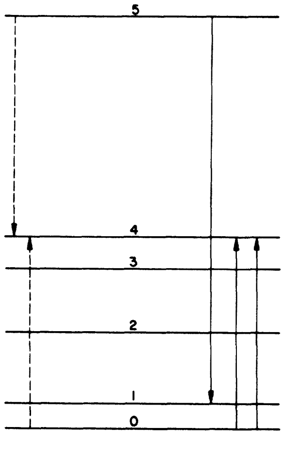

FIG. 1. Typical energy levels for enhanced three-particle process (solid arrows) if two-particle process (dashed arrows) is not quite resonant.

tremely sharp resonances, $\rho(E)$ is proportional to n.] Finally, both factors tend to make multiparticle processes relatively more important.

(d) The solutions of the nonlinear rate equations (22) associate with each transition probability $\langle W\rangle$ a concentration dependence which reflects the number of particles interacting in a given microscopic process. The usual two-particle resonance is characterized by an n^2 dependence, and a general Q-particle process would be characterized by a n^Q dependence. This is in conflict with the theory used by Van Uitert and co-workers,[27-38] by Holloway and co-workers,[65,67] by Axe and Weller,[66] and by others. There, one associates the concentration dependence with the electric multipole order of the interaction, in such a way that, if the spatial dependence of the interaction is r^{-p}, then $\langle W\rangle$ has associated with it a factor $n^{p/3}$. Since the concentration dependence of the transfer process has been the subject of voluminous investigation, we dwell on this point in some detail.

First, the $\langle W\rangle$ which we have defined in Eq. (21), and which enters as a parameter in Eq. (22), exhibits no concentration dependence that can be linked with a coordinate dependence. For $w_{ij}=r_{ij}^{-p}$,

$$\langle W\rangle=\int_{r_0}^{\infty} r^{-p}\,4\pi r^2 dr=(3/p^{-3})\,r_0^{-p}v_0\ , \tag{36}$$

where r_0 is a unit lattice cell dimension and v_0 is $\frac{4}{3}\pi r_0^3$. We note that r_0^{-p} reflects a dependence on a geometrical lattice distance, not on the average particle separation. Suppose now that we introduce (incorrectly) the constraint that the interaction must occur with the nearest available atom. Using the nearest-neighbor distribution derived by Chandrasekhar,[115] we have

$$\langle W\rangle=\int_{r_0}^{\infty} r^{-p}\,e^{-4\pi r^3 n/3}\,4\pi r^2 dr=r_0^{-p}v_0E_{p/3}(v_0 n)\ , \tag{37}$$

where $E_{p/3}(x)$ is an incomplete γ function,[116,117] and once again the r_0^{-p} dependence reflects the lattice dimension only. The incomplete γ function does contain a concentration dependence. Expanding $\langle W\rangle$ in ascending powers of the concentration, one obtains a series in integer powers, the leading term of which is always a constant, (except that one fractional power, namely, $n^{p/2-1}$, will also be present). The leading term for general p is

$$\lim_{n\to 0}\langle W\rangle=\frac{3}{p^{-3}}\,r_0^{-p}v_0\ , \tag{38}$$

in agreement with Eq. (36). To give an example of the other terms in the series, for $p=8$ the first few terms are

$$\langle W\rangle=r_0^{-8}v_0\,[0.6-1.5\,nv_0+26.9\,(nv_0)^{5/3}-1.5\,(nv_0)^2+0.5\,(nv_0)^3\cdots]\ . \tag{39}$$

We stress again that the concentration dependence beyond the leading term in Eqs. (37) and (39) arises only from artificially constraining the interaction to the nearest available atom.

The concentration dependence of the yield η or of the transfer efficiency $(1-\eta)$ is discussed in Sec. V.

V. YIELD

The directly measured quantity is usually not $\langle W\rangle$, but the yield η, or the relative yield η/η_0. One either measures decays following a pumping pulse, or one measures intensities under steady-state conditions.

Forster and others have calculated the yield, on the basis of the FCIH model, for transient decays. If $n(t)$ is the decaying population of the fluorescent state, then the yield is defined as

$$\eta(t)=\int_0^{\infty} n(t)\,dt\ , \tag{40}$$

and the relative yield is defined

$$\eta/\eta_0=\eta\Big/\int_0^{\infty} n_0(t)\,dt\ , \tag{41}$$

where $n_0(t)$ is the population with transfer absent. Forster has used Eq. (41) in conjunction with various spatial dependences for $w(\vec{r})$, namely, the Perrin interaction[1] (hard sphere), the Stern-Volmer interaction[118] ($W=\text{const}$), and the dipole-dipole interaction ($W\sim r^{-6}$). Colbow has applied the same scheme to exchange interaction ($W\sim e^{-r/r_0}$), and Inokuti and Hirayama have generalized to arbitrary inverse powers of r.

It is usually assumed that the transient definition of yield will apply to steady-state conditions as well. This is true within the assumptions of the FCIH model, but it is not true in general. We examine this point in more detail.

Suppose the decay of the population n is described by a linear equation of the form

$$Ln=0\ , \tag{42}$$

where L is a linear operator. Then one can define a Green's function $G(t)$ which satisfies

$$LG=\delta(t)\ , \tag{43}$$

where $\delta(t)$ is the δ function. For a general excitation $p(t)$, $n(t)$ will be given by

$$n(t)=\int p(t')\,G(t-t')\,dt'\ . \tag{44}$$

Defining the Fourier transform as usual as

$$F(\omega)=\int_{-\infty}^{\infty} e^{i\omega t}F(t)\,dt\ , \tag{45}$$

one transforms Eq. (44) to

$$n(\omega)=p(\omega)\,G(\omega)\ . \tag{46}$$

In particular, for the steady state $\omega=0$, one obtains from Eqs. (46) and (45)

$$n_{ss}=p_{ss}\int_{-\infty}^{\infty} G(t)\,dt\ . \tag{47}$$

Equation (47) establishes the identity between the steady-state yield and the transient yield by identifying $n(t)$ following a pulse with the Green's function. It is now clear what the requirements are for this equivalence:

(i) The response must be linear. If the response is governed by nonlinear terms, the equivalence will definitely not hold.

(ii) In the transient mode, the pulse must be short compared with any other time in the problem. (This requirement in some circumstances conflicts with the need to produce a signal of sufficient strength so that its decay can be accurately measured.)

It is easy to multiply examples where the above conditions are not met, and to which the expressions for the yield of FCIH systems do not apply. We illustrate with a schematic example. Consider the nonlinear equation for the decay of x,

$$\dot{x} = -W_{\mathrm{tr}}\, x^2 - W_D x \; , \tag{48}$$

and the associated steady-state equation

$$0 = -W_{\mathrm{tr}}\, x^2 - W_D x + W_P \; . \tag{49}$$

For yield defined as the time integral of the transient following a pulse,

$$\frac{\eta}{\eta_0} = \frac{W_D}{W_{\mathrm{tr}}\, x_0} \ln\left(\frac{W_{\mathrm{tr}}\, x_0 + W_D}{W_D}\right) \; . \tag{50}$$

For yield defined as steady-state emission,

$$\eta/\eta_0 = (1/2y)\left[-1 + (1+4y)^{1/2}\right] \; , \tag{51a}$$

$$y = W_{\mathrm{tr}}\, W_P / W_D^2 \; . \tag{51b}$$

These two functions are, of course, quite different, and depend in a nonlinear way on the intensity of the original excitation. If we now consider the linearized form of Eqs. (48) and (49), replacing x^2 by $2x$, then both definitions yield the same result, namely,

$$\eta/\eta_0 = W_D/(W_D + 2W_{\mathrm{tr}}) \; . \tag{52}$$

Equations (50)–(52) are plotted in Fig. 2, but we defer discussion of this figure.

Dexter's calculation of the transfer efficiency η_T,

$$\eta_T = 1 - \eta/\eta_0 \; , \tag{53}$$

interprets expressions such as Eq. (52) as applicable separately to each sensitizer and its partner activator. One then averages over separations, constraining the interaction artificially to the nearest available neighbors. Such a procedure would seem to require the following assumptions: (a) The process is linear. (b) There is only one set of resonant pairs in the energy structure. These two conditions are necessary for the correctness of a form such as Eq. (52). (c) Each activator-sensitizer pair is a separate and isolated system within which the transfer process occurs. (d) The constraint to nearest neighbors goes still further, and it is not clear why it is justifiable in principle. It probably does not introduce great error for very low concentrations. With Dexter, we then have

$$\eta_T = \int_{r_0}^{\infty} \frac{W_{\mathrm{tr}}(r)}{W_D + W_{\mathrm{tr}}(r)}\, e^{-4\pi r^3 n/3}\, 4\pi r^2\, dr \; . \tag{54}$$

For $W \sim r^{-6}$, this integral is readily evaluated and is

$$\eta_T = -v_c \,\mathrm{Im}\left[e^{inv_c} E_1\,(nv_0 + inv_c)\right] \; , \tag{55}$$

where E_1 is again an incomplete γ function, v_0 is the volume per lattice site, and v_c is a critical volume such that for r_c defined by $v_c = \frac{4}{3}\pi r_c^3$, $W_{\mathrm{tr}}(r_c) = W_D$. The quantities nv_0 and nv_c correspond, respectively, to Dexter's $x_a C^+ v_0$ and y. The result quoted by Dexter is the limit of expression (55) for large v_c/v_0. If one expands the result in Eq. (55) in powers of n, one obtains, exactly as with $\langle W \rangle$ in Sec. IV, an ascending series in integer powers, the leading term of which is a constant.

What happens if we remove the constraint to nearest neighbors? We then have

$$\eta_T = \int_{r_0}^{\infty} \frac{W_{\mathrm{tr}}(r)}{W_D + W_{\mathrm{tr}}(r)}\, 4\pi r^2\, dr \; . \tag{56}$$

The value of this integral for all even $p > 4$ is

$$3v_0 \left\{ \frac{\pi}{p \sin(3\pi/p)} + \frac{2}{p} \sum_{j=1}^{p/2} \left[\ln\left(\sin\frac{\pi(2j-1)}{2p}\right) \cos\frac{3\pi(2j-1)}{p} - \frac{\pi(2j-1)}{2p} \sin\frac{3\pi(2j-1)}{p} \right] \right\} , \tag{57}$$

and is identical with the leading concentration-independent term of the expansion of Eq. (55). The concentration dependence of Dexter's result is thus due exclusively to the constraint to nearest neighbors.

The conclusion to be drawn from this is not that the FCIH model really predicts a concentration-independent transfer efficiency, but rather that the special assumptions underlying (54) are not tenable. Specifically, it seems that the model of nearest-neighbor pairs interacting as closed and isolated systems must be rejected. This is underscored by what happens when the same method is consistently applied to quenching interactions. In place of (56) one would then obtain

$$\eta_Q = \int_{r_0}^{\infty} \frac{W_D}{W_D + W_{\mathrm{tr}}(r)}\, 4\pi r^2\, dr \; , \tag{58}$$

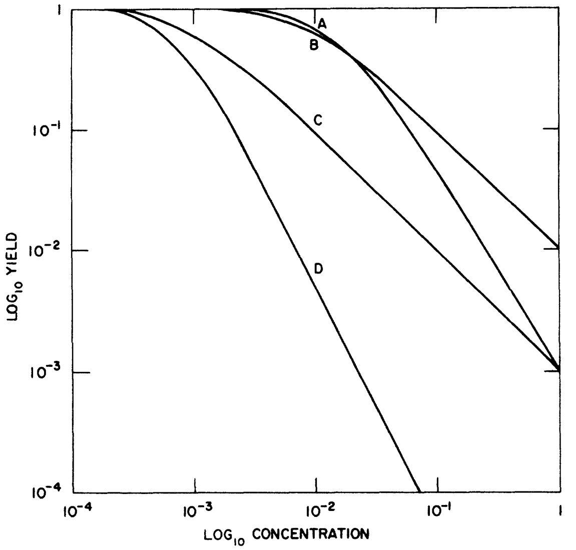

FIG. 2. Yield for schematic model (48), (49): curve A—transient yield, $x_0 = 0.01$; curves B and C—steady-state yield, $W_p = 1$ and $W_p = 100$; curve D—linearized yield.

which diverges for all physical interactions, long range and short range. The reason for this is that quenching means precisely that particles within the same system interact with one another, and is in direct conflict with the requirement for isolation.

We have so far discussed yield with special reference to the FCIH model. We now look at yield when the rate-equation approximation is valid. One great advantage of this model is that it permits dealing with the nonlinear nature of the process, a feature that is precluded at the outset within the FCIH model. If the process is described by macroscopic rate equations, it is of course simply a matter of solving these equations to obtain both the time-dependent and steady-state populations, and any functions dependent on them. Such a solution may present formidable technical difficulties, even with computers, but conceptually it is quite unambiguous.

Nevertheless, a few comments are instructive. For nonlinear systems, the transient decay will depend on the initial conditions. If the system is excited by a pulse, the decay will depend qualitatively, and not just by a scale factor, on the intensity and length of the pulse. In the steady state, the emission will depend nonlinearly on the pump power. In our schematic model, Eqs. (48) and (49), the transient yield (50), and steady-state yield (51) are not only different from one another but depend, respectively, on $x(0)$ and W_p which reflect excitation conditions.

In Fig. 2 we show yield as a function of concentration, based on our schematic model. We have taken $W_D = 100$ and $W_{\mathrm{tr}} = 10^8 n^2$, as arbitrary and not unreasonable values. Curve A is for the transient yield taking $x_0 = 0.01$. Curves B and C are for steady-state yield taking $W_p = 1$ and 100, respectively. Curve D is the linearized yield (52). A log-log plot tends to suppress differences between functions. Nevertheless one striking difference is the break point. For the transient yield, the break point is $n^2 = (W_D / W_{\mathrm{tr}}) x_0^{-1}$, for the steady-state yield it is $n^2 = (W_D / W_{\mathrm{tr}})(W_D / W_p)$, and for the linearized yield it is $n^2 = 0.5(W_D / W_{\mathrm{tr}})$. Curves A and B both break at $n = 0.01$, curves C and D at $n = 0.001$. We note that the break point depends on the excitation level (e.g., B and C) when nonlinearities are important. But even with identical break points, the shapes at the knee and even the asymptotic behaviors are different for different definitions of yield. Of course our example is schematic, but it illustrates the main points.

We also show, in Fig. 3, the decays associated with Eq. (48) if the system is excited by a short pulse. The pulse intensity is reflected in the initial population x_0 of the excited state $(0 < x_0 < 1)$. The condition $x_0 n^2 < W_{\mathrm{tr}} / W_D$ (curve A) produces decays that are exponential on a time scale W_D^{-1}. The condition $x_0 n^2 > W_{\mathrm{tr}} / W_D$ (curve C) produces nonexponential decays. In curve B, $x_0 n^2 = W_{\mathrm{tr}} / W_D$ and the nonexponentiality is just observable. Although the details are simplistic, the essentials are typical of nonlinear relaxations. Both the excitation history and the concentration determine the character of the curves, and a critical condition can be defined which marks the onset of nonlinearity, on some characteristic time scale. We note the qualitative similarity of the curves of Fig. 3 to FCIH decays with multipole interactions.

For concentrations low enough and transfer probabilities small enough so that the nonlinear equations can be linearized, a form similar to (52) will usually be found in simple cases. The appropriate average is

$$\eta / \eta_0 = \langle W_{\mathrm{tr}} \rangle / (W_D + \langle W_{\mathrm{tr}} \rangle) , \tag{59}$$

i.e., one averages W over the system first, a procedure which is, of course, explicit in the derivation of the rate equations. In the quenching situation, the relative intensity, in simple cases, will have a form such as

$$I / I_0 = W_D / (W_D + \langle W_{\mathrm{tr}} \rangle) . \tag{60}$$

In either case, the concentration dependence is the ratio of two polynomials, since a power of n is associated with W_{tr}.

We note that Dexter has deduced an equation of the form (60) by an intuitive argument. Nevertheless, expressions such as (59) and (54) rest on extreme opposite physical models.

Equations of the form (59) and (60) approximately fit many experiments, with W_{tr} proportional to a

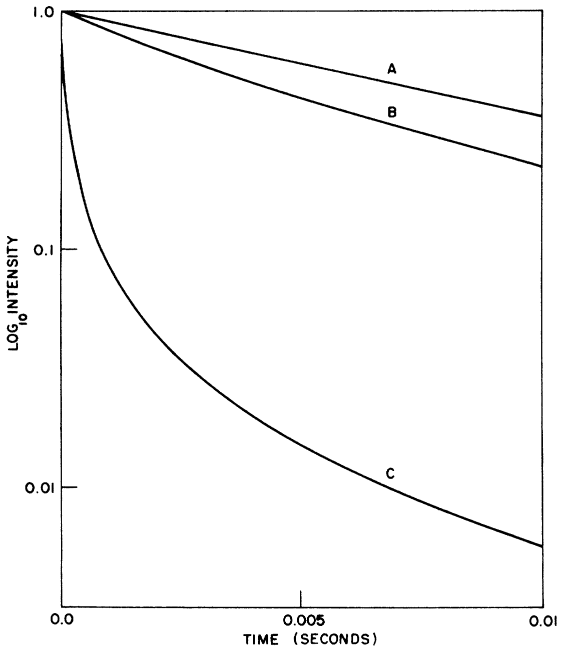

FIG. 3. Decay for schematic model (48), (49): curve A—$x_0 n^2 < W_{\text{tr}}/W_D$; curve B—$x_0 n^2 = W_{\text{tr}}/W_D$; curve C—$x_0 n^2 > W_{\text{tr}}/W_D$.

power of n between 2 and 3. We propose that the interpretation of this fact is that two-particle processes are by far the most probable, followed by three-particle processes. As explained in Sec. IV, both can also occur together. We feel this is a more satisfying interpretation than the association of concentration dependence with multipole orders. First, the low powers of concentration characterize transfers involving metastable levels, which are very-high-order forbidden and which require high-order multipoles. Dexter showed that such multipoles are far more effective in coupling particles to particles than to radiation, and more recent work[21,85] again enhances this contention. Second, the association of powers of the concentration with multipole orders does not emerge from a consistent treatment of yield under any model. Third, the evidence seems to be that, at least for rare-earth impurities in many inorganic crystals, the conditions of the rate-equation approximation are satisfied. We shall discuss these points further below.

VI. SUMMARY

The main purpose of this paper has been to clarify the origin and meaning of the equations that enter the theory of luminescent transfer, and to clarify the relation between experimental observations and the parameters entering these equations.

We have related the equations to first principles of quantum statistics and relaxation theory. We have done this in two steps—by deriving equations first for microscopic spatial probability distributions, and from these distributions deriving equations for macroscopically observable probabilities or populations. If a given system distributes energy internally in a time short compared with transfer to another system, then kinetic nonlinear rate equations apply. If the opposite is true, and if in addition the microscopic equations can be linearized, the FCIH equations apply in suitable circumstances.

We found that the averaged transition probabilities $\langle W\rangle$, which enter as parameters into the rate equations, depend on powers of the concentration, and that these powers reflect the number of particles participating in one transfer. The form of the interaction will affect the magnitude of $\langle W\rangle$ but not its concentration dependence. Not only two, but any number of particles can participate in a single process. This lack of restriction greatly increases the possibilities for resonance. We showed that an inhibited $(Q-1)$-particle resonance tends to make a Q-particle resonance highly probable.

We found that the Forster method for computing yield is specific to the FCIH model. The Dexter computation, on the other hand, implies constraints that are too stringent to be sustained in most of the applications where one would like to use it. For the rate-equation model, the yield is found in terms of the solutions of the rate equations. For nonlinear rate equations, the excitation conditions will enter functionally. The concentration dependence of the yield in the FCIH model is slightly sensitive to the form of the interaction, but in the rate-equation model it is sensitive only to the number of particles in one transfer, through $\langle W\rangle$. In neither model is there an association between multipoles of the interaction potential and powers of the concentration.

The nature of the interaction is most directly accessible to experiment, not through concentration dependence, but through the angular dependence of selection rules. Such experiments have been pursued particularly by Filipescu and coworkers[58–62] and by Keller.[77] For short-range interactions, the angular dependence of wave-function overlaps gives direct information, and some of the experiments of Blasse[43,46] allow interpretation of this kind.

We now indicate some of the evidence that the rate-equation approximation is indeed appropriate for many rare-earth systems in inorganic materials. An adequate treatment of the experimental literature would require a monumental review article. All we can do is sketch some of the arguments:

(i) From their lifetime studies of rare earths in trichloride crystals,[119] Gandrud and Moos conclude that typically 4×10^5 transfers within the rare-earth system occur before a trap is reached. A trap is an activator in reverse, and the kinetics are symmetric. This would indicate intrasystem transfer between pairs of resonant levels more rapid than intersystem transfer by an overwhelming factor, in these materials. The same conclusion has been drawn on the basis of more indirect evidence for certain rare-earth systems in glass.[69,70]

(ii) Actually, the Gandrud and Moos study provides a lower limit on the intrasystem transfer rate considered in this paper. Intrasystem transfer occurs most commonly and most rapidly between pairs of *identical* levels, which are, of course, in perfect resonance. Now the transition probability has a peak at exact resonance, and this peak can be very large for two-particle processes if inhomogeneous broadening is small.

(iii) Where the rate equations have been used to interpret experiment,[42,68,73,75,81,82,84,93] they have given a satisfactory account of the data.

(iv) The preponderance of n^2 and n^3 dependences of the yield is *prima facie* evidence of the correctness of expressions similar to schematic equation (60) which represents a rate-equation model. The appearance of a critical concentration or break point in the yield curve has commonly been interpreted in terms of the Dexter calculation,[43,57,89] but, in fact, this feature is common to all models. On the other hand, there are cases[78] which exhibit a power-law dependence but for which the FCIH model cannot give a good fit for any assumed interaction.

(v) If one attempts to interpret powers of the concentration as a multipole index, although there seems to be no theoretical reason to do this, the n^2 and n^3 dependences cannot be reconciled with the matrix elements for forbidden transitions, such as occur, for instance, between pairs of metastable levels.

(vi) Regarding nonexponential decays: (a) Nonexponential decays are a consequence of either the FCIH model or the rate-equation model. Even linearized rate equations can give apparently nonexponential decays, because multiple exponentials are notoriously difficult to distinguish from true nonlinearities. (The FCIH model itself falls into this category in a limiting sense, as composed of N exponentials.) (b) Most experimental (Refs. 27, 30, 33, 36, 68, 71–73, 75, 79, 83, 84, 86, 89, 91, 93, and 94) decays appear ambiguous in this respect without a detailed analysis. Such analysis would include the corresponding steady-state data, data concerning temperature dependence, and data from directly related transfers, and it would consider the relative strength of various hypotheses. (c) Without impugning the FCIH model, we suggest that in a significant class of systems the rate-equation model forms a more consistent and more natural framework for the data, including nonexponential decays.

(vii) Analysis such as we have just indicated will be the subject of a subsequent paper.

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[*] Senior Research Associate, National Research Council.

[1] F. Perrin, Compt. Rend. 192, 1727 (1931).

[2] T. Forster, Ann. Physik 2, 55 (1948).

[3] T. Forster, *Fluoreszenz Organische Verbindungen* (Vandenhoeck and Ruprecht, Göttingen, 1951).

[4] T. Forster, Z. Elektrochem. 53, 93 (1949).

[5] T. Forster, Z. Naturforsch. 4a, 321 (1949).

[6] T. Forster, Discussions Faraday Soc. 27, 7 (1959).

[7] D. L. Dexter, J. Chem. Phys. 21, 836 (1952).

[8] D. L. Dexter and J. H. Schulman, J. Chem. Phys. 22, 1063 (1954).

[9] D. L. Dexter, Phys. Rev. 126, 1962 (1962).

[10] D. L. Dexter, J. Chem. Phys. 47, 1379 (1967).

[11] M. Trlifaj, Czech. J. Phys. 9, 4 (1959).

[12] M. Trlifaj, Czech. J. Phys. 8, 510 (1958).

[13] M. Trlifaj, Czech. J. Phys. 6, 533 (1956).

[14] G. W. Robinson and R. P. Frosch, J. Chem. Phys. 38, 1187 (1962).

[15] V. F. Chel'tsov, Zh. Eksperim. i Teor. Fiz. 47, 567 (1964) [Sov. Phys. JETP 20, 376 (1965)].

[16] K. Colbow, Phys. Rev. 139, A274 (1965).

[17] M. Inokuti and H. Hirayama, J. Chem. Phys. 43, 1978 (1965).

[18] K. Colbow, Phys. Rev. 141, 742 (1966).

[19] J. Lavorel, J. Chem. Phys. 47, 2235 (1967).

[20] M. Yokota and O. Tanimoto, J. Phys. Soc. Japan 22, 779 (1967).

[21] W. P. Wolf and R. J. Birgenau, Phys. Rev. 166, 376 (1967).

[22] J. Avery and J. Packer, in *Proceedings of the International Symposium on the Triple State, Beirut* (Cambridge U. P., Cambridge, England, 1967), p. 47.

[23] R. Orbach and M. Tachiki, Phys. Rev. 158, 524 (1967).

[24] R. S. Knox, Physica 39, 361 (1968).

[25] R. J. Birgenau, J. Chem. Phys. 50, 4282 (1969).

[26] R. G. Delosh and W. J. C. Grant, Phys. Rev. B 1, 1754 (1970).

[27] L. G. Van Uitert, in *Luminescence of Inorganic Solids*, edited by P. Goldberg (Academic, New York, 1966), p. 465. Note that this review article contains extensive reference to the literature covering inorganic wide gap insulators prior to 1966.

[28] L. G. Van Uitert and L. F. Kojnson, J. Chem. Phys. 44, 3514 (1966).

[29] L. F. Johnson, J. E. Geusic, and L. G. Van Uitert, Appl. Phys. Letters 8, 200 (1966).

[30] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 44, 1578 (1966).

[31] L. G. Van Uitert, E. F. Dearborn, and H. M. Marcos, Appl. Phys. Letters 9, 255 (1966).

[32] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 46, 3551 (1967).

[33] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 46, 420 (1967).

[34] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 47, 547 (1967).

[35] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 47, 1595 (1967).

[36] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 47, 3653 (1967).

[37] L. G. Van Uitert, J. Electrochem. Soc. 114, 4400 (1968).

[38] L. G. Van Uitert, E. F. Dearborn, and W. H. Grodkiewicz, J. Chem. Phys. 49, 4400 (1968).

[39] L. G. Van Uitert, S. Singh, H. J. Levinstein, L. F. Johnson, W. H. Grodkiewicz, and J. E. Geusic, Appl. Phys. Letters 15, 53 (1969).

[40] L. G. Van Uitert, H. J. Levinstein, and W. H. Grodkiewicz, Mat. Res. Bull. 4, 381 (1969).

[41] L. H. Johnson, J. E. Geusic, H. J. Grodkiewicz, T. Kushida, S. Singh, and L. G. Van Uitert, Appl. Phys. Letters 15, 48 (1969).

[42] J. P. Van der Ziel, L. G. Van Uitert, and W. H. Grodkiewicz, J. Appl. Phys. 41, 3308 (1970).

[43] G. Blasse, J. Chem. Phys. 45, 2356 (1966).

[44] G. Blasse and A. Bril, Phys. Letters 23, 440 (1966).

[45] W. Wannamaker, A. Bril, J. W. te Wugt, and J. Broos, Philips Res. Repts. 21, 270 (1966).

[46] G. Blasse, J. Chem. Phys. 46, 2583 (1967).

[47] G. Blasse and A. Bril, J. Chem. Phys. 47, 5139 (1967).

[48] G. Blasse and A. Bril, J. Inorg. Nucl. Chem. 31, 1521 (1967).

[49] G. Blasse and A. Bril, Phys. Status Solidi 20, 551 (1967).

[50] G. Blasse and A. Bril, Philips Res. Repts. 22, 46 (1967).

[51] G. Blasse and J. deVries, J. Electrochem. Soc. 114, 875 (1967).

[52] A. Bril, G. Blasse, and J. A. Bertens, J. Electrochem. Soc. 115, 395 (1968).

[53] G. Blasse and A. Bril, J. Electrochem. Soc. 115, 1067 (1968).

[54] G. Blasse, Philips Res. Repts. 23, 344 (1968).

[55] G. Blasse, Phys. Letters 28A, 444 (1968).

[56] G. Blasse, Philips Res. Repts. 24, 131 (1969).

[57] G. Blasse, J. Luminescence 2, 766 (1970).

[58] J. R. DeMenter and N. Filipescu, J. Am. Chem. Soc. 90, 6425 (1968).

[59] N. Filipescu, in *Molecular Luminescence*, edited by E. C. Lim (Benjamin, New York, 1969), p. 697.

[60] N. Filipescu, J. R. DeMenter, and F. L. Minn, J. Am. Chem. Soc. 91, 4169 (1969).

[61] N. Filipescu and J. R. DeMenter, J. Chem. Soc. 38B, 616 (1969).

[62] N. Filipescu, J. Luminescence 1, 489 (1970).

[63] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters 7, 442 (1961).

[64] F. Varsanyi, Phys. Rev. Letters 11, 314 (1963).

[65] W. W. Holloway, M. Kestigian, and R. Newman, Phys. Rev. Letters 11, 458 (1963).

[66] J. D. Axe and P. F. Weller, J. Chem. Phys. 40, 3006 (1964).

[67] W. W. Holloway and M. Kestigian, J. Chem. Phys. 13, 147 (1965).

[68] C. Asawa and G. W. Robinson, Phys. Rev. 141, 251 (1966).

[69] A. D. Pearson and G. E. Peterson, Appl. Phys. Letters 8, 210 (1966).

[70] A. D. Pearson, G. E. Peterson, and W. P. Northover, J. Appl. Phys. 37, 729 (1966).

[71] E. Nakasawa and S. Shionoya, J. Chem. Phys. 47, 3211 (1967).

[72] V. F. Ergova, V. Zubkova, G. Kareptyan, and A. Mak, Opt. i Spektroskopiya 23, 275 (1967) [Opt. Spectry. (USSR) 23, 148 (1967)].

[73] A. Alaam and B. DiBartolo, J. Chem. Phys. 47, 3790 (1967).

[74] S. C. Sen and H. N. Bose, Z. Physik 201, 368 (1967).

[75] C. Asawa, Phys. Rev. 155, 188 (1967).

[76] J. B. Birks and S. Georghiou, J. Phys. B 1, 958 (1968).

[77] R. A. Keller, J. Am. Chem. Soc. 90, 1940 (1968).

[78] J. S. Stroud, Appl. Opt. 7, 751 (1968).

[79] N. Mataga, H. Obashi, and T. Okada, J. Phys. Chem. 73, 370 (1969).

[80] F. Klement and Ch. Lushchik, A. Prik. Spektrosk. (USSR) 8, 545 (1968). Note that this review article contains extensive reference to the Russian literature prior to 1968.

[81] V. Belous, Opt. i Spektroskopiya 24, 751 (1968) [Opt. Spectry. (USSR) 24, 308 (1968)].

[82] V. Belous, Opt. i Spektroskopiya 24, 586 (1968) [Opt. Spectry. (USSR) 24, 308 (1968)].

[83] Yu. K. Voronko, M. V. Dmitruk, V. V. Osiko, and V. T. Udorenchik, Zh. Eksperim. i. Teor. Fiz. 54, 751 (1968) [Sov. Phys. JETP 27, 197 (1968)].

[84] R. C. Powell, Phys. Rev. 173, 358 (1968).

[85] R. J. Birgenau, Appl. Phys. Letters 13, 193 (1968).

[86] J. B. Birks, in *Molecular Luminescence*, edited by E. C. Lim (Benjamin, New York, 1969).

[87] B. I. Bykovski and V. F. Pisarenko, Opt. i Spektroskopiya 26, 487 (1969) [Opt. Spectry. (USSR) 26, 271 (1969)].

[88] V. L. Levshin, N. D. Maksimova, and R. K. Pirinchieva, Opt. i Spektroskopiya 26, 127 (1969) [Opt. Spectry. (USSR) 26, 70 (1969)].

[89] Yu. K. Voronko, V. V. Osiko, and I. A. Scherbakov, Zh. Eksperim. i Teor. Fiz. 55, 1598 (1968) [Sov. Phys. JETP 28, 838 (1969)].

[90] N. A. Tolstoi, A. P. Abramov, and I. Ya. Grerlovin, Fiz. Tverd. Tela 11, 2644 (1969) [Sov. Phys. Solid State 11, 2644 (1969)].

[91] J. Appleson, G. F. Garlick, W. E. Lamb, B. Lunn, Phys. Status Solidi 34, 537 (1969).

[92] V. R. Belan, Ch. M. Briskina, V. V. Grigoryants, and M. E. Zhaborinski, Zh. Eksperim. i Teor. Fiz. 57, 1148 (1969) [Sov. Phys. JETP 30, 627 (1970)].

[93] J. D. Kingsley, J. Appl. Phys. 41, 175 (1970).

[94] H. Nishimura, M. Tanaka, and M. Tomura, J. Phys. Soc. Japan 28, 128 (1970).

[95] K. A. Wickersheim and R. A. Buchanan, Appl. Phys. Letters 17, 184 (1970).

[96] R. G. Tolman, *The Principles of Statistics Mechanics* (Oxford U. P., Oxford, England, 1938).

[97] For a review article, see G. V. Chester, Repts. Progr. Phys. 26, 411 (1963).

[98] E. W. Montroll, in *Lectures in Theoretical Physics*, edited by W. E. Brittin and L. G. Dunham (Interscience, New York, 1960), Vol. 3, p. 221.

[99] P. M. Mathews, I. I. Shapiro, and D. L. Falkoff, Phys. Rev. 120, 1 (1960).

[100] D. L. Falkoff, in *Lectures on the Many Body Prob-*

lem, edited by E. R. Caianello (Academic, New York, 1963), Vol. I.

[101]M. Kac, *Lectures on Probability Theory* (Interscience, New York, 1959).

[102]J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940).

[103]W. J. C. Grant, Phys. Rev. 135, A715 (1964).

[104]H. Margenau, Phys. Rev. 48, 755 (1935).

[105]H. Margenau and J. Watson, Rev. Mod. Phys. 8, 22 (1936).

[106]P. W. Anderson, J. Phys. Soc. Japan 9, 316 (1954).

[107]W. J. C. Grant, Phys. Rev. 135, A727 (1964).

[108]W. J. C. Grant, Phys. Rev. 134, A1554 (1964).

[109]L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, New York, 1968).

[110]P. S. Pershan, Phys. Rev. 117, 109 (1960).

[111]W. J. C. Grant, Phys. Rev. 134, A1565 (1964).

[112]W. J. C. Grant, Phys. Rev. 134, A1574 (1964).

[113]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[114]*Fluctuations, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haas (Plenum, New York, 1962).

[115]S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

[116]*Higher Transcendental Functions* (*Bateman Manuscript Project*), edited by A. Erdelyi (McGraw-Hill, New York, 1953), Vol. 2.

[117]L. W. Busbridge, Quart. J. Math. Oxford 1, 176 (1950).

[118]O. Stern and M. Volmer, Z. Physik 20, 183 (1919).

[119]W. B. Gandrud and H. W. Moos, J. Chem. Phys. 49, 2170 (1968).