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Resonance Energy Transfer in Condensed Media from a Many-Particle Viewpoint*

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The Förster-Dexter (FD) theory of transfer of electronic energy by the resonance interaction between an excitation localized at one impurity and an unexcited state at another is based on a model consisting of an ensemble of inert continuous dielectric hosts in each of which are imbedded one sensitizer and one activator at random positions; there are only two relevant electronic energy levels associated with each impurity, and these levels are merely broadened by lattice vibrations. In spite of the apparently crude approximations involved in the two-impurity model for resonance transfer, the FD theory has been vital to the understanding of energy-transfer phenomena in solids, liquids, and biological systems, and most of the predictions of the theory have been verified at least semiquantitatively. Clearly the two-impurity model must not be so crude as it appears to be at first glance, and many of the complicated effects which one might expect from a more elegant theory must be hidden in the parameters of the model. In this paper, the resonance-energy-transfer mechanism is treated from a many-particle viewpoint, and the collective nature of the excitation migration is taken into account. Assuming a nonmagnetic monatomic crystal with two substitutional impurities, the initial and final states of the energy-transfer process are taken to be localized excitons, or excited states of the entire system of impurities plus host crystal. First, on a linear-chain model it is found that the host states modify the bare interaction between impurities and also provide a short-ranged virtual-exciton mechanism for energy transfer. Then the long-ranged part of the effective interaction is treated for a three-dimensional model of a tight-binding crystal, with the effects of the impurities on the host treated within the framework of linear response theory. For long-ranged excitation migration, the connection between the collective picture and the two-impurity picture is established by performing a unitary transformation on the crystal Hamiltonian and showing that an effective two-atom Hamiltonian consistent with the FD theory can be extracted from it. Therefore, the two-impurity picture of sensitized luminescence is shown to be a suitable limit of a many-body treatment of migration of localized excitons; and, in this limit, all the effects of the medium can be included in a simple frequency-dependent dielectric response function. The approximations implicit in the FD theory are discussed, with particular attention paid to the effects of low-lying host-crystal states on the rate of energy migration. It is argued that the usual weak-coupling criterion is not sufficient to guarantee the validity of the FD theory and that multiple-scattering effects not included in the theory become important at relatively low concentrations.

I. INTRODUCTION

EXCITONIC energy migration in condensed media, which is characterized by a net transfer of electronic energy without attendant charge transport, is thought to be responsible for a variety of phenomena in physics, chemistry, and biology ranging from sensitized luminescence to photosynthesis.[1,2] Perhaps the simplest systems in which exciton energy transfer can be investigated experimentally are crystalline insulators lightly doped with two different kinds of impurities; in such cases, a localized excited state can be prepared on one impurity center and the excitation energy can hop to a nearby impurity of the second species, using the Coulomb interaction between the two centers as the jump-inducing perturbation. If the localized exciton resides on the first center long enough for the surrounding lattice to completely relax about it, the migration mechanism is referred to as "resonance energy transfer" or "inductive resonance."[3–5]

The current theoretical understanding of resonance-transfer phenomena in solids is due primarily to Förster and Dexter, who provided a sound basis for the theories of sensitized luminescence and concentration quenching and depolarization of fluorescence. The basic difference between the Förster-Dexter (FD) theory and earlier unsuccessful attempts to explain sensitized luminescence in solids and liquids[6] was that the effects of lattice relaxation around the excited impurities were adequately accounted for, albeit somewhat phenomenologically. In treating the phonons correctly, Förster and Dexter had actually converted the earlier resonance theories into a theory of energy transfer dominated by *nonresonance* transitions between the vibrational energy levels of

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[1] Th. Förster, *Fluoreszenz Organischer Verbindungen* (Vandenhoeck and Ruprecht, Göttingen, Germany, 1951).

[2] D. L. Dexter and R. S. Knox, *Excitons* (Interscience Publishers, Inc., New York, 1965); R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963). The mobile generalized excitons defined here differ from the conventional static-lattice excitons in that they may contain admixtures of lattice and molecular vibrations and may be localized about impurity molecules.

[3] Th. Förster, Naturwiss, **33**, 166 (1946); Ann. Physik **2**, 55 (1948); Z. Naturforsch. **4A**, 321 (1949).

[4] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

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

[6] J. Perrin, *Deuxième Conseil de Chêmie Solvay* (Gauthier-Villars, Paris, 1925), p. 322; Compt. Rend. Acad. Sci. (C. R. Hebd. Séances Acad. Sci.) **184**, 1097 (1927); F. Perrin, Ann. Chim. Phys. **17**, 283 (1932); S. I. Vavilov, J. Phys. (USSR) **7**, 141 (1943).

electronic states whose vibrational bands overlapped. As a result of the misnomer "resonance energy transfer" there was considerable confusion about the validity of first-order perturbation theory in their analysis, a point that has only recently been clarified by Robinson and Frosch.[7]

Most of the efforts to refine and extend the original FD theory have been based on the FD model of two highly-localized molecule-like impurities imbedded in an inert, continuous dielectric host in such a way that the electronic energy levels are merely broadened by the host's lattice vibrations.[8,9] However, a proper theoretical model of the resonance-energy-transfer mechanism should account for the *collective* nature of the process, treating the initial and final states as *localized excitons* or excited states of the entire system of impurities *plus* host crystal and allowing for the electronic polarization of the medium. The connection between the collective picture and the two-molecule picture is by no means obvious.[10] The primary goal of this paper will be to demonstrate that connection, and to account for the effects of the host medium on resonance transfer between two impurities. In particular, energy transfer over short distances will be treated in terms of a linear-chain model of a solid with two substitutional impurities, and it will be shown that host electronic states significantly enhance short-ranged energy migration between impurities. The resonance energy transfer over large distances will be considered on the basis of a realistic tight-binding model of a crystal; it will be demonstrated that the FD theory of resonance transfer can be obtained as a suitable limit of a many-body treatment of migration of localized excitons, and that, in this limit, all the effects of the medium can be included in a simple dielectric response function. In addition, the approximations implicit in the Förster-Dexter theory will be formally discussed, with particular attention paid to their experimental implications.

Section II will be devoted to a brief review of the FD theory, and Sec. III will deal with energy transfer over short distances in a static lattice and includes a discussion of energy transfer in a model one-dimensional system. Section IV is concerned with long-ranged energy migration and contains the derivation of the effective FD Hamiltonian. Section V summarizes our findings.

II. REVIEW OF FÖRSTER-DEXTER THEORY

A successful theory of resonance energy transfer and impurity-sensitized luminescence in solids and liquids was first formulated by Förster, who was primarily interested in excitation migration between organic molecules whose electronic dipole transition moments are large.[3] Dexter subsequently extended Förster's dipole-dipole theory to include the effects of dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, and exchange interactions, all of which are important in inorganic systems where the impurity transitions of interest are often forbidden.[4,5]

The model system on which the FD theory is based consists of two impurities,[11] a sensitizer or donor (S) and an activator or acceptor (A), imbedded in an inert insulating isotropic host. The effects of finite concentrations of impurities are accounted for by performing an ensemble average over all possible positions of S and A. Here it is assumed that the excited sensitizer has only two possible channels for decay: radiative emission or radiationless resonance transfer of its excitation to A (single-center radiationless transitions, cascade processes, and mechanisms of energy transfer involving a net transport of charge are neglected)[12]; likewise, radiationless decay of S is assumed to occur with negligible probability.[13]

The physical processes occurring during sensitized luminescence have been discussed by Dexter.[4] Here we are interested in the resonance transfer, but it is important to remember that the initial and final excited states are well-defined as a result of rapid lattice relaxation about S and A, respectively, which localizes the excitation at one impurity or the other. The resonance transition may be treated by first-order time-dependent perturbation theory (Fermi's Golden Rule),

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[7] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **37**, 1962 (1962); **38**, 1187 (1963). Because of the lattice vibrations, it is incorrect to diagonalize the electronic Hamiltonian (Ref. 6) and correct to treat the interaction between impurities by perturbation theory.

[8] J. D. Axe and P. F. Weller, J. Chem. Phys. **43**, 1 (1965); M. Inokuti and F. Hirayama, *ibid.* **43**, 1978 (1965), and references therein; K. B. Eisenthal and S. Siegel, *ibid.* **41**, 652 (1964); Yu. A. Kurskii and A. S. Selivanenko, Opt. i Spektroskopiya **8**, 643 (1960) [English transl.: Opt. Spectry. (USSR) **8**, 340 (1960)]; M. D. Galanin, Zh. Eksperim. i Teor. Fiz. **28**, 485 (1955) [English transl.: Soviet Phys.—JETP **1**, 317 (1955)].

[9] For a survey of the literature concerning resonance transfer, see *Luminescence of Inorganic Solids*, edited by P. Goldberg (Academic Press Inc., New York, 1967); F. R. Lipsett, *Energy Transfer in Polyacene Solid Solutions* (National Research Council of Canada, Ottawa, 1957 and 1961); Th. Förster, in *Modern Quantum Chemistry*, edited by O. Sinanoglu (Academic Press Inc., New York, 1965), Part III; L. N. M. Duysens, Progr. Biophys. **14**, 1 (1964); and Refs. 10 and 15.

[10] *Luminescence of Organic and Inorganic Materials*, edited by H. P. Kallmann and G. M. Spruch (John Wiley & Sons, Inc., New York, 1962), pp. 296 *et seq.*; *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith, and J. L. Magee (John Wiley & Sons, Inc., New York, 1960), p. 322.

[11] In what follows, we restrict ourselves to the case of impurities S and A randomly distributed throughout the host. Hence "high concentration" is equivalent to "small S-A separation." However, in organic systems especially, the S's and A's are not necessarily randomly distributed, but often occupy specific sites on a macromolecule, so that the average S-A separation is fixed; in fact, such fixed-distance experiments provide the most conclusive verification to date of the FD dipole-dipole transfer rate $P_{SA}=R_{dd}^6/(\tau_S R^6)$. See L. Stryer and R. P. Haugland, Proc. Natl. Acad. Sci. (U. S.) **58**, 719 (1967); S. A. Latt, H. T. Cheung, and E. R. Blout, J. Am. Chem. Soc. **87**:**5**, 995 (1965); K. H. Drexhage, M. M. Zwick, and H. Kuhn, Ber. Bursenges. Phys. Chem. **67**, 62 (1963).

[12] See Ref. 15 for a discussion of these assumptions.

[13] The results can be generalized to the case of S's fluorescence efficiency less than unity simply by replacing τ_S in Eq. (4) with the observed lifetime divided by the fluorescence efficiency of an isolated S. (We assume that S's radiationless relaxation time is long compared with the S-A transfer time, and that the radiationless relaxation rate divided by the radiative rate is a constant for all transition energies E.)

provided that (a) the "weak-coupling" criterion[14] is satisfied so that the time for transfer is very much longer than typical phonon relaxation times; (b) the Stokes's shifts of both impurities are sufficiently large that the activator emission band has negligible energy overlap with the sensitizer absorption, thereby rendering back-transfer inefficient[4]; and (c) impurity concentrations are sufficiently weak that interactions (i) between sensitizers, (ii) between activators, and (iii) between sensitizers and activators—other than the excited S and its nearest-neighboring activator—are all negligible.[15] We shall discuss these conditions later and shall find that they are often violated in even the "best" resonance-transfer experiments.

Assuming that the Golden Rule is applicable, and taking the effective Hamiltonian to be a sum of atomic Hamiltonians for S and A plus an effective interaction term H', the energy migration rate P_{SA} from an initial state with excitation localized at S to a final state with the energy residing on A is

$$P_{SA}=(2\pi/\hbar)\,|\langle s,a^*,v_s,v^*_a|H'|s^*,a,v^*_s,v_a\rangle|^2 \times\delta(w_s+w^*_a-w^*_s-w_a). \quad (1)$$

Here the initial state $|i\rangle\equiv|s^*,\,a,\,v^*_s,\,v_a\rangle$ is specified by the electronic and vibrational quantum numbers s^* and v^*_s of the excited sensitizer and the activator quantum numbers a and v_a; similar notation holds for the final state $|f\rangle\equiv|s,\,a^*,\,v_s,\,v^*_a\rangle$, and w^*_s and w_s (w^*_a and w_a) denote the zero-order atomic plus vibrational energies of the sensitizer (activator); and the Dirac δ function ensures conservation of energy. The perturbation Hamiltonian H' can be expanded in a multipole series which is, neglecting terms of higher order than quadrupole-quadrupole,

$$\begin{aligned} H'=&\{e^2/\epsilon R^3\}\{\mathbf{M}_S\cdot\mathbf{M}_A-3(\mathbf{M}_S\cdot\hat{R})(\mathbf{M}_A\cdot\hat{R})\}\\ &+\{e^2/\epsilon R^4\}\{\tfrac{5}{2}(\hat{R}\cdot\mathbf{Q}_A\cdot\hat{R})(\mathbf{M}_S\cdot\hat{R})-\mathbf{M}_S\cdot\mathbf{Q}_A\cdot\hat{R}\}\\ &+\{e^2/\epsilon R^4\}\{\tfrac{5}{2}(\hat{R}\cdot\mathbf{Q}_S\cdot\hat{R})(\mathbf{M}_A\cdot\hat{R})-\mathbf{M}_A\cdot\mathbf{Q}_S\cdot\hat{R}\}\\ &+\{e^2/\epsilon R^5\}\{\hat{R}\cdot\mathbf{Q}_A\cdot\mathbf{Q}_S\cdot\hat{R}+\tfrac{1}{4}(\hat{R}\cdot\mathbf{Q}_A\cdot\hat{R})(\hat{R}\cdot\mathbf{Q}_S\cdot\hat{R})\\ &\qquad+\tfrac{1}{6}\mathbf{Q}_A:\mathbf{Q}_S\}. \end{aligned} \quad (2)$$

Here $\mathbf{M}_A$ and $\mathbf{Q}_A$ are the dipole and quadrupole moment operators, respectively, of the activator atom:

$$\mathbf{M}_A\equiv\sum_{\nu=1}^{Z(A)}\mathbf{r}_{A\nu},\quad \mathbf{Q}_A\equiv3\mathbf{M}_A\mathbf{M}_A-\mathbf{M}_A\cdot\mathbf{M}_A\mathbf{1}\,,$$

with similar notation for S. The vector $\mathbf{R}\equiv R\hat{R}$ is the internuclear separation, e is the electronic charge, and ϵ is the "dielectric constant of the host." Averaging the square of the perturbation Hamiltonian over all directions $\hat{R}$[16] and also over the relative orientation of $\mathbf{M}_S$ and $\mathbf{M}_A$, neglecting terms in H' other than the dipole-dipole interaction, summing P_{SA} [Eq. (1)] over initial states, and averaging over final states, we obtain the average dipole-dipole resonance transition rate

$$\begin{aligned} \bar{P}_{SA}(dd)=&\frac{2\pi}{\hbar}\int dE\,\frac{e^2}{\epsilon^2R^6}|\Phi_{dd}|^2\Big[\sum_{s^*,s}g^{-1}(s^*)\int dw^*_s\\ &\times p(v^*_s)\rho_S(w^*_s-E)\,|\langle s|M_S|s^*\rangle|^2|(s,v_s|s^*,v_s^*)|^2\Big]\\ &\times\Big[\sum_{a^*,a}g^{-1}(a^*)\int dw_a p(v_a)\rho_A(w_a+E)\\ &\qquad\times|\langle a^*|M_A|a\rangle|^2|(a^*,v^*_a|a,v_a)|^2\Big]. \end{aligned} \quad (3)$$

Here E is the energy of the transition ($\equiv w^*_s-w_s$); $|\Phi_{dd}|^2$ is the averaged angular factor (equal to $\frac{2}{3}$); $g(s^*)$ is the degeneracy of the atomic electronic state $|s^*\rangle$; $p(v^*_s)dw^*_s$ is the probability that the excited sensitizer is in the vibrational state $|v^*_s)$ with energy w^*_s; $\rho_S(w)$ is the density of sensitizer final states at energy w; and $(s,v_s|s^*,v^*_s)$ is a Franck-Condon overlap factor. Similar notation holds for A. We have taken the initial- and final-state wave functions to be products of non-overlapping single-atom functions centered on S and A, respectively, with the lattice vibrations accounted for in the Born-Oppenheimer approximation; furthermore, we have assumed that the electronic parts of the matrix elements are insensitive to the details of the vibrational factors and so may be evaluated at the equilibrium lattice configuration (Condon approximation).[17]

The angular averaging has allowed us to factor the transition rate into two independent parts; if an isolated excited S undergoes only radiative transitions, the sensitizer factor is proportional to the S emission intensity divided by its emission lifetime τ_S; likewise, the activator factor is proportional to A's absorption cross section. Thus, in the FD theory, the transition elements are related to absorption and emission data, and $\bar{P}_{SA}\,(dd)$ is written

$$\bar{P}_{SA}(dd)=(1/\tau_S)(R_{dd}{}^6/R^6)\,,$$

where

$$R_{dd}{}^6\equiv\int\frac{9\hbar^4c^4}{8\pi}\,\frac{|\Phi_{dd}|^2}{\epsilon^2}Q^0{}_A\frac{f_S(E)F_A(E)}{E^4}dE \quad (4)$$

is the "critical transfer distance" at which spontaneous emission and resonance transfer to A are equally probable decay channels for S. Here $Q^0{}_A$ is the area under the activator absorption band [i.e., in terms of the cross section, $Q^0{}_A\equiv\int\sigma_A(E)dE$], $F_A(E)$ is the activator absorption normalized to unity, $f_S(E)$ is the

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[14] W. T. Simpson and D. L. Peterson, J. Chem. Phys. **26**, 588 (1957); Th. Förster, in *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith, and J. L. Magee (John Wiley & Sons, Inc., New York, 1960), pp. 300–319.

[15] J. D. Dow, Ph.D. thesis, University of Rochester, 1967 (unpublished); available from University Microfilms, Ann Arbor, Michigan.

[16] Normally this averaging procedure would occur later in the calculation anyway.

[17] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

normalized S emission, and c is the speed of light *in vacuo*. We emphasize that the averaging procedure can only be valid if the distance R is so large that the (exact) wave functions of the impurities (in the absence of the direct interaction H') are uncorrelated and that, even then, the averaging of $|\langle i|\mathbf{M}_S\cdot\mathbf{M}_A|f\rangle|^2$ is suspect. The large-R requirement is in effect an *extremely weak coupling* requirement which turns out to be considerably more restrictive than the usual weak-coupling criterion.[14] We shall return to this point later.

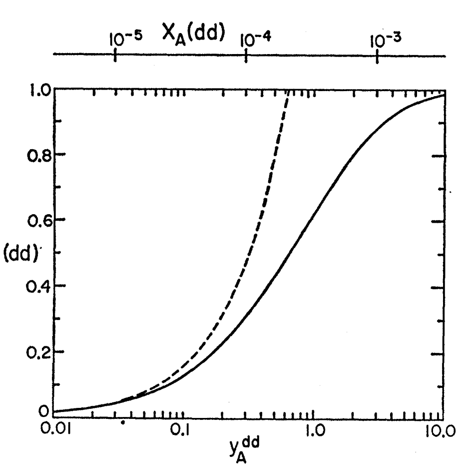

FIG. 1. Quantum yield for dipole-dipole resonance transfer as a function of reduced activator concentration $y_A{}^{dd}$. The solid line is obtained by assuming that an excited S donates its energy to the nearest A only, while the dashed line represents the contribution to $\bar{\eta}_T(dd)$ which is linear in $y_A{}^{dd}$. Where the two lines coincide, the FD two-impurity model is applicable; at larger concentrations, multiple-scattering effects are important, and the solid line should be viewed as an interpolation formula which gives the correct value of $\bar{\eta}_T(dd)$ in the high-concentration limit. Typical values of $x_A(dd)$ are listed above the plot.

The observable quantity associated with a resonance transfer of energy is efficiency of transfer from S or transfer quantum yield $\bar{\eta}_T$:

$$\bar{\eta}_T=\frac{\bar{P}_{SA}\tau_S}{\bar{P}_{SA}\tau_S+1}=\frac{R_{dd}{}^6}{R_{dd}{}^6+R^6}\,. \tag{5}$$

For experiments on doped crystals, $\bar{\eta}_T$ must be averaged over all possible values of R to provide an expression for $\bar{\eta}_T$ as a function of activator concentration. The appropriate weight for this average is the probability

$$\begin{aligned} q(R)&=4\pi R^2x_AC_A(1-x_A)^{4\pi R^3C_A/3}\\ &\approx 4\pi R^2x_AC_Ae^{-4\pi R^3x_AC_A/3} \end{aligned} \tag{6}$$

that the nearest activator is a distance R away from a given sensitizer.[4,18] Thus we have

$$\begin{aligned} \bar{\eta}_T(dd)&=y_A{}^{dd}\,\mathrm{Ci}(y_A{}^{dd})\,\sin y_A{}^{dd}-y_A{}^{dd}\,\mathrm{Si}(y_A{}^{dd})\,\cos y_A{}^{dd}\\ &=\tfrac{1}{2}\pi y_A{}^{dd}+O((y_A{}^{dd})^2)\approx\tfrac{2}{3}\pi^2R_{dd}{}^3x_AC_A\,, \end{aligned} \tag{7}$$

where the reduced concentration for dipole-dipole transfer $y_A{}^{dd}$ is equal to $\frac{4}{3}\pi R_{dd}{}^3x_AC_A$, C_A is the density of sites available to activators, x_A is the probability that a particular one of these sites is occupied by an activator, and Ci(y) and Si(y) are the cosine- and sine-integral functions.[19] Since the two-atom model on which the FD theory is based omits competition between activators for the excitation of a given sensitizer, the average quantum yield for transfer from S *must be linear in the activator concentration.* The nonlinear terms in Eq. (7) arise from the invalid assumption that energy is transferred to the nearest-neighbor activator *only* and should be regarded as providing merely an interpolation formula for $\bar{\eta}_T$ which is valid in the high-concentration limit ($x_A\rightarrow 1$). Thus it is incorrect to interpret data which are nonlinear in x_A (e.g., as in concentration quenching experiments) in terms of the FD two-impurity theory. An adequate theory of resonance transfer in heavily doped crystals would have to treat the multiple scattering effects which arise from interactions between activators. Note that sensitizer concentrations must be small, since we have implicitly assumed that the total number of transitions is pro-

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[18] A great deal of effort has been expended on the averaging problem: R. A. Cellarius, Photochem. Photobiol. **6**, 91 (1967); M. Inokuti and F. Hirayama, J. Chem. Phys. **43**, 1978 (1965); A. G. Tweet, W. D. Bellamy, and G. L. Gaines, Jr., *ibid.* **41**, 2068 (1964); M. D. Galanin, Zh. Eksperim. i Teor. Fiz. **28**, 485 (1955) [English transl.: Soviet Phys.—JETP **1**, 317 (1955)]; A. Ore, J. Chem. Phys. **31**, 442 (1959); **33**, 31 (1960); B. Ya. Sveshnikov, Dokl. Akad. Nauk SSSR **111**, 78 (1956) [English transl.: Soviet Phys.—Doklady **1**, 633 (1957)]; L. N. M. Duysens, Progr. Biophys. **14**, 1 (1964); M. Leibowitz, J. Chem. Phys. **69**, 1061 (1965); M. Z. Maksimov and I. M. Rozman, Opt. i Spektroskopiya **12**, 606 (1962) [English transl.: Opt. Spectry. (USSR) **12**, 337 (1962)]; I. M. Rozman, *ibid.* **10**, 354 (1961) [English transl.: Opt. Spectry. (USSR) **10**, 178 (1961)]. A number of authors have argued that the average over impurity distributions should not be performed at this point of the calculation or in this manner. For the most part, their arguments are meant to apply to impurity concentrations such that two or more activators can compete for the excitation of a single sensitizer. We understand the underlying assumptions of their arguments to be that (a) the FD theory applies in this regime and (b) the net rate of transfer of energy from a given S is the sum of transition rates to each A (with no interference terms). However, the FD theory is based on a two-impurity model and does not apply to systems with high impurity concentrations; first-order perturbation theory may be used to calculate a decay rate only if one decay channel is overwhelmingly favored by the system (e.g., transfer to the nearest A); and interference and multiple-scattering effects become dominant at high concentrations (e.g., $x_A\approx 1$). Therefore we feel quite content to perform the average as Dexter did, fully realizing that the results are only meaningful at low concentrations and that even then we must allow for 33% fluctuations in the average nearest-neighbor distance.

Förster and Dexter were both keenly aware of the limitations of the theory at high impurity concentrations and they, as well as others (Ore, Cellarius), attempted to overcome these problems, which we can trace to two causes: (a) the failure of the two-impurity model to adequately describe multiple scattering at high concentrations (unless damping effects are included, second-order perturbation theory diverges for transfer from S to A by way of an intermediate state localized at another activator); and (b) the incorrectness of the effective Hamiltonian H' at short distances R (linear-response theory breaks down, the concept of an effective interaction becomes meaningless, and virtual-exciton transfer becomes important). We discuss (b) below; clearly a satisfactory extension of the FD theory to overcome (a) or (b) must be a many-particle theory.

[19] *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, Washington, D. C., 1964), Natl. Bur. Stds. Appl. Math. Ser. **55**, 231.

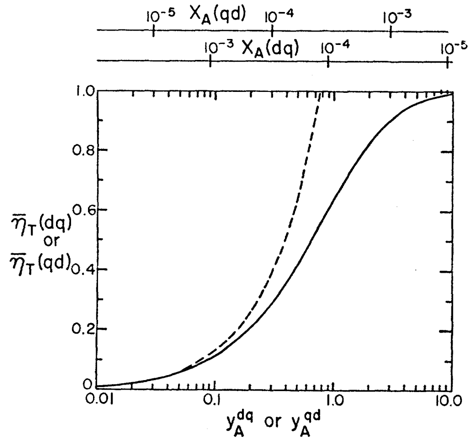

FIG. 2. Quantum yields for dipole-quadrupole and quadrupole-dipole transfer as a function of reduced concentration y_A.

portional to the concentration of excited sensitizers. The quantum yield for dipole-dipole transfer Eq. (7) is graphed in Fig. 1 as a function of $y_A{}^{dd}$. The dotted line represents the term linear in $y_A{}^{dd}$, while the solid line is the result for nearest-neighbor transfer only. Where the two lines coincide, the two-atom model is applicable; while at higher concentrations, the model fails and it is necessary to hypothesize that only transfer to the nearest activator is possible in order to get the interpolation formula provided by the solid line. For the sake of easy reference, typical values of x_A are indicated in the abscissa above the plot.

The corresponding transition rates and quantum yields for dipole-quadrupole (dq) and quadrupole-quadrupole (qq) transfer are

$$\begin{aligned}\bar{P}_{SA}(dq)&=\frac{1}{\tau_S}\frac{R_{dq}{}^8}{R^8},\\ \bar{\eta}_T(dq)&=\frac{\pi^2R_{dq}{}^3x_AC_A}{2\sin\frac{3}{8}\pi}+O(x_A{}^2),\\ \bar{P}_{SA}(qq)&=\frac{1}{\tau_S}\frac{R_{qq}{}^{10}}{R^{10}},\end{aligned}\tag{8}$$

and

$$\bar{\eta}_T(qq)=\frac{2\pi^2R_{qq}{}^3x_AC_A}{5\sin\frac{3}{10}\pi}+O(x_A{}^2),$$

where $R_{dq}{}^8$, $R_{qd}{}^8$, and $R_{qq}{}^{10}$ may be expressed in terms of the absorption and emission spectra for the single impurities S and A, as in Eq. (4) for $R_{dd}{}^6$. Since quadrupole absorption data are not always easily measured, it is sometimes necessary to guess the absorption spectra from a knowledge of the more-easily measured emission data.[4] The quantum yields for dipole-quadrupole and quadrupole-quadrupole transfer are presented in Figs. 2 and 3.

A careful inspection of Eqs. (4) and (8) reveals that the transition rates may be generally written

$$\bar{P}_{SA}=(2\pi/\hbar)\,|\Delta_{\text{eff}}|^2\rho_F\,,\tag{9}$$

where Δ_{eff} is the effective electronic factor in the transition matrix element [$\Delta_{\text{eff}}=\Delta/\epsilon$ here, where Δ is the bare electronic matrix element and ϵ is the (high-frequency) dielectric constant of the medium], and ρ_F is the vibrational overlap of the normalized activator absorption spectrum with the normalized sensitizer emission. Thus the electronic states determine the strength of the bare interaction, polarization effects reduce this interaction, and the lattice vibrations merely provide an effective density-of-final-states factor in the transition rate.

There are three effects of the medium which apparently have not been included in Eq. (9): (a) local-field corrections [e.g., in the case of the interaction between point-dipole impurities in a static cubic crystal, the perturbation H' of Eq. (2) is not $M_AM_B\Phi_{dd}/\epsilon R^3$ but $((\epsilon+2)/3)^2M_AM_S\Phi_{dd}/\epsilon R^3$, where $\frac{1}{3}(\epsilon+2)$ is the Lorentz local-field factor[20,21]]; (b) the effects of the index of refraction; and (c) the possibility that the medium could severely alter the radial dependence of the interaction. In general, the local-field factor is a complicated function of the dielectric constant, the radii of the excited states of the impurities, and local lattice distortion. In a quantum-mechanical treatment of the full crystal Hamiltonian, the local-field correction arises from distortion of the free-atom-like impurity wave functions as a result of interactions between the impurity and its neighbors.[22] Thus, if the unperturbed initial and final states are eigenstates of the crystal Hamiltonian minus the sensitizer-activator interaction, then the local field is included in matrix elements evaluated experimentally.[23] Hence local-field corrections are already included in P_{SA}.[24] With regard to (b), in evaluating the transition matrix elements by relating them to absorption and emission probabilities, there appear factors of $n(E)$, the index of refraction evaluated at the transition energy. These factors account for reduced photon velocity in the crystal and the altered density of photon states. For the dipole-diople interaction, it turns out that they cancel, so that no factors of $n(E)$ appear in R_{dd}. This cancellation does not occur for higher-multipole interactions, however.[4,15,21,23] Finally, with regard to (c), the medium could alter the radial dependence of the interaction; e.g., an indirect

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[20] G. D. Mahan, Phys. Rev. **153**, 983 (1967).

[21] Note that Dexter's original definition (Ref. 3) of local field contains an extra factor κ^{-1}; the more conventional definitions are used in Refs. 15, 20, and 23.

[22] D. L. Dexter, Phys. Rev. **101**, 48 (1956); R. F. Guertin and F. Stern, *ibid.* **134**, A427 (1964).

[23] W. B. Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962); J. Chem. Phys. **43**, 1768 (1965); M. Lax and E. B. Burstein, Phys. Rev. **97**, 39 (1955).

[24] It will become apparent later that this is only true if the impurities are sufficiently separated that the long-wavelength components of the interaction are dominant [$\epsilon(q,\omega)\approx\epsilon(0,\omega)$].

interaction between S and A exists in that both impurities couple to the host-exciton bands as a result of interactions with their neighbors. On physical grounds, we expect that such indirect coupling is small whenever R is large or the excited impurity states lie far below the host-exciton bands. In Sec. III, we shall demonstrate the correctness of this expectation, but we shall show that typical separations R and impurity-host energy differences are sufficiently small to make the indirect coupling important in most resonance-transfer experiments.

III. ENERGY TRANSFER IN A STATIC LATTICE

In the preceding section, we saw that the primary effect of lattice vibrations on the resonance transfer of energy is to determine a density-of-states factor. With this in mind, we now consider the case of energy transfer in a static lattice in order to determine the effects of host-exciton states on the bare-interaction matrix element. The indirect coupling of S and A through the intermediate exciton states provides a mechanism for energy transfer, as first pointed out by Agranovich.[25] Such virtual-exciton migration is a strong-coupling mechanism of energy transfer in the sense that S and A are each strongly coupled to a nearest-neighbor host atom and each host is strongly coupled to another; it is a weak-coupling mechanism in the sense that the effective indirect interaction between S and A is small compared with $\hbar/\tau_{ve}$, where τ_{ve} is a typical vibrational equilibration time. For S-A separations less than the mean free path of a host exciton immersed in a bath of lattice vibrations, it is a satisfactory approximation to compute an effective interaction matrix element Δ_{eff} neglecting the phonons and then to determine the energy migration rate using the Golden Rule [Eq. (9)].

The mathematical technique that we shall use to calculate Δ_{eff} is the method of classical Green's functions developed by Lifshitz[26] and others[27] for the treatment of localized perturbations. Thus we shall generalize Agranovich's second-order calculation for impurities near a polymer chain to the case of impurities in a three-dimensional crystal, allowing for a direct interaction between impurities and including (at least formally) the contributions to virtual-exciton migration from all orders of perturbation theory. In order to get a qualitative feeling for the effects of virtual-exciton migration, we shall ultimately specialize to the case of a one-dimensional crystal, in which case our calculation becomes mathematically similar to the two vibrational mass defects treated by Montroll and Potts.[28] We emphasize that the formalism of this section can be applied to real crystals, the most serious problem being the calculation of a perfect-crystal Green's function; such a calculation would not be appreciably more difficult than the many band-structure computations that are now regarded as routine. Our choice of one-dimensional Hamiltonian[29] is similar to those of a number of authors[30] who have considered impurities in a static lattice; but the interpretation of our results is drastically different. The quantity of interest in all energy-migration calculations is the probability that an excitation initially localized at S may be found at site A at time t. In our calculations, we assert that this probability is $\bar{P}_{SA}t$ [with $\bar{P}_{SA}$ given by Eq. (9)], thereby including phonons *a posteriori* in accordance with the weak-coupling nature of the FD theory; thus we need only calculate the strength of the effective interaction Δ_{eff} for a static lattice. On the other hand, it is sometimes possible to calculate the desired transition probability directly; however, many-phonon processes must be included in order to obtain a probability which increases linearly in time (as experimental data demand); a static-lattice computation overlooks the

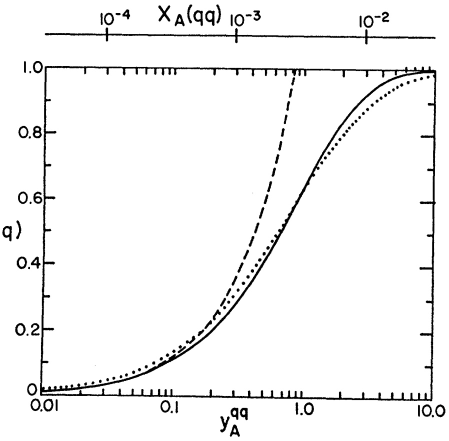

FIG. 3. Quantum yield for quadrupole-quadrupole resonance transfer. The notation is the same as in Fig. 1, except that the dotted line is added. The dotted line represents $\bar{\eta}_T$ for dipole-dipole nearest-neighbor transfer plotted as though $y_A{}^{dd}=y_A{}^{qq}$, and illustrates how difficult it is to discern among dd, dq, and qq mechanisms (the dq and qd lines would lie even closer to the solid line), even if transfer to nearest neighbors is the only kind to occur.

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[25] V. M. Agranovich, Opt. i Spektroskopiya **9**, 113 (1960); **9**, 798 (1960) [English transls.: Opt. Spectry. (USSR) **9**, 59 (1960); **9**, 421 (1960)].

[26] I. M. Lifshitz, Nuovo Cimento Suppl. 10, **3**, 716 (1963).

[27] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3, and references therein.

[28] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956).

[29] E. Bartholomé and E. Teller, Zeit. Physik. Chem. **B19**, 3 (1931); K. F. Herzfeld, J. Chem. Phys. **10**, 508 (1942); H. M. McConnell, *ibid.* **35**, 508 (1961); G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954); M. Lax, *ibid.* **94**, 1391 (1954); A. Morita and M. Azuma, J. Phys. Soc. Japan **18**, 1273 (1963); E. I. Rashba, Opt. i Spektroskopiya **2**, 568 (1957) [English transl.: AEC-tr-5967].

[30] R. E. Merrifield, J. Chem. Phys. **38**, 290 (1963); S. Takeno, *ibid.* **44**, 853 (1966); D. P. Craig and M. R. Philpott, Proc. Roy. Soc. (London) **A290**, 602 (1966); **A293**, 213 (1966); K. Katsuura and M. Inokuti, J. Chem. Phys. **41**, 989 (1964).

weak-coupling nature of resonance transfer and results in a temporally oscillating probability.

We consider a static simple cubic crystal of N atoms whose ground-state wave functions are S-like with P-like excited states in the energy interval of interest (all higher excited states being neglected) and assume that the elementary excitations of the crystal are in one-to-one correspondence with the excitations of the same crystal with infinite lattice constant. The perfect-crystal Hamiltonian is taken to be

$$H_0=\sum_{n=1}^{N} H_1(n)+\sum_{n}^{N} \sum_{<\, m}^{N} H_2(n,m),$$

where $H_1(n)$ is the atomic Hamiltonian of the host atom at lattice point R_n:

$$H_1(n)=\sum_{\nu=1}^{Z(n)}\left\{\frac{-\hbar^2}{2m}\nabla^2{}_{n\nu}-\frac{Z(n)e^2}{|\mathbf{r}_{n\nu}-\mathbf{R}_n|}\right\}+\tfrac{1}{2}\sum_{\mu=1\ (\mu\neq\nu)}^{Z(n)}\frac{e^2}{|\mathbf{r}_{n\nu}-\mathbf{r}_{n\mu}|},\tag{10}$$

where $-eZ(n)$ is the nuclear charge of the nth atom and $\mathbf{r}_{n\nu}$ is the position operator of the electron $n\nu$. $H_2(m,m)$ is the interatomic coupling

$$H_2(n,m)=\sum_{\nu=1}^{Z(n)}\sum_{\mu=1}^{Z(m)}\frac{e^2}{|\mathbf{r}_{n\nu}-\mathbf{r}_{m\mu}|}-\sum_{\mu=1}^{Z(m)}\frac{Z(n)e^2}{|\mathbf{r}_{m\mu}-\mathbf{R}_n|}-\sum_{\nu=1}^{Z(n)}\frac{Z(m)e^2}{|\mathbf{r}_{n\nu}-\mathbf{R}_m|}+\frac{Z(n)Z(m)e^2}{|\mathbf{R}_n-\mathbf{R}_m|},\tag{11}$$

which may be written in the dipole-dipole approximation as

$$H_2(n,m)\approx\frac{\mathbf{M}_n\cdot\mathbf{M}_m}{R_{nm}{}^3}-\frac{3\mathbf{M}_n\cdot\mathbf{R}_{nm}\mathbf{R}_{nm}\cdot\mathbf{M}_m}{R_{nm}{}^5}.\tag{12}$$

Here $\mathbf{R}_{nm}\equiv\mathbf{R}_n-\mathbf{R}_m$ and $M_n=\sum_{\nu=1}^{Z(n)}e\mathbf{r}_{n\nu}$. The Schrödinger equation for the perfect crystal is $H_0|\ \rangle=E_0|\ \rangle$, with solutions

$$|\lambda\rangle,\ E_0(\lambda)\,.\tag{13}$$

For a tight-binding crystal made up of atoms with the second excited states energetically distant from the first, it is often satisfactory to approximate the solutions of Eq. (13) by appropriately antisymmetrized linear combinations of products of atomic wave functions.[31] The gound state is then formed from all the atomic ground states, and the low-lying excited state $|n,\gamma\rangle$ localized at site n is formed from an atomic excited state γ (γ labels the three P states) on site n and all other atoms in the ground state. The set of states $|n,\gamma\rangle$ do not diagonalize H_0, but the unperturbed exciton wave functions[2] $|\mathbf{k},\gamma\rangle$ formed as coherent linear combinations of the $|n,\gamma\rangle$ do effect the diagonalization:

$$|\mathbf{k},\gamma\rangle=N^{-1/2}\sum_{n}|n,\gamma\rangle\exp(i\mathbf{k}\cdot\mathbf{R}_n)\,,\tag{14}$$

$$E_0{}^{\gamma}(\mathbf{k})=\sum_{n}\langle n',\gamma|H_0|n,\gamma\rangle\exp[i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_{n'})].\tag{15}$$

Here $\mathbf{k}$ lies in the first Brillouin zone, and we have imposed periodic boundary conditions. If we neglect configuration interaction and consider only states with one excited atomic function, then the elementary excitation spectrum of the static crystal is determined by the band-structure equation (15).

Assuming that we have found satisfactory solutions for the pure crystal, we introduce two impurities, one at the origin ($n=S$) and the other at $n=A$; we assume that both impurities have S-like ground states and P-like excited states. Thus we have a new Hamiltonian

$$H=H_0+V\,,\tag{16}$$

where V contains terms for the differences between impurity and host free-atom Hamiltonians and also changes in interatomic coupling. In order to simplify the mathematics, we restrict ourselves for the moment to the case of two identical impurities, each with a symmetrical ground (atomic) state and a low-lying vector-like excited state. We wish to obtain the effective interaction between an excited state of the crystal localized at S and an unexcited state at A; that is (for identical impurities), one-half the splitting between the excited-state energies. Thus we look for the solutions of the Schrödinger equation

$$H|\ \rangle=E|\ \rangle=H_0+V|\ \rangle\tag{17}$$

with energies below the lowest-lying host-crystal energies. (We assume that the impurity levels lie in the transparent region of the host's spectrum.) Equation (17) is more conveniently written

$$|\ \rangle=(E-H_0)^{-1}V|\ \rangle=gV|\ \rangle,\tag{18}$$

and the impurity-state eigenvalues are the solutions of

$$\det(\mathbf{1}-gV)=0\,,\tag{19}$$

where $\mathbf{1}$ is the unit operator and we have introduced the classical Green's function of the *perfect* crystal

$$g(E)=(E-H_0)^{-1}=\sum_{\lambda}\frac{|\lambda\rangle\langle\lambda|}{E-E_0(\lambda)}\,.\tag{20}$$

Equation (19) is easily solved if a set of basis functions can be found in which V (and hence gV) has only a few sizable matrix elements. In general, there will be two sets of nearly threefold degenerate excited impurity energies which solve Eq. (19); the degeneracy, which results from the fact that cubic crystals do not split P-like atomic states, being slightly removed by V. If we consider the case of identical impurities, S and A,

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[31] R. S. Knox, J. Phys. Chem. Solids **9**, 238 (1959); A. Gold, Phys. Rev. **124**, 1740 (1961).

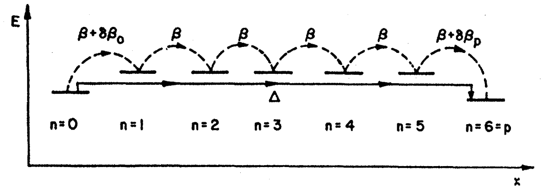

FIG. 4. Energy-level diagram showing a direct interaction (solid line) and an indirect interaction (dashed line) between two impurities separated by six lattice spacings in a one-dimensional crystal.

then the effective interaction between an excited S atom and an unexcited A atom is half the splitting between the centers of gravity of the (now degenerate) sets of impurity energies.

In order to gain a qualitative understanding of the host crystal's effects on the net S-A interaction and how the host states alter the resonance-transfer rate, we specialize to the case of a one-dimensional nonmagnetic crystal in which excited-state interatomic matrix elements are large only between nearest neighbors,[32] $\langle n|H_0|n\pm1\rangle\equiv\beta=\langle n\pm1|H_0|n\rangle$; the diagonal elements of the unperturbed Hamiltonian are $\langle n|H_0|n\rangle\equiv\alpha$ and the ground-state energy is taken to be zero; all other matrix elements are taken to be zero. The perturbation due to the two impurities is determined by its matrix elements between localized states of the unperturbed crystal:

$$\langle S|V|S\rangle\equiv\delta\alpha=\langle A|V|A\rangle,$$

$$\langle A|V|S\rangle\equiv\Delta=\langle S|V|A\rangle,$$

$$\langle S\pm1|V|S\rangle\equiv\delta\beta_0=\langle S|V|S\pm1\rangle,$$

and

$$\langle A|V|A\pm1\rangle\equiv\delta\beta_p=\langle A\pm1|V|A\rangle.$$

For simplicity S and A are assumed to have identical matrix elements ($\delta\beta_0=\delta\beta_p\equiv\delta\beta$), and the ground-state energy of the perturbed crystal is assumed to be the same as for the unperturbed crystal.

This model Hamiltonian provides (a) a direct interaction Δ between impurities and (b) an indirect interaction which results from coupling of both impurities to intermediate exciton states of the host crystal. Thus energy can migrate from S to A in a single hop or by a succession of virtual hops from one atom to its neighbor; these processes are represented on an energy-level diagram in Fig. 4 and in terms of Feynman diagrams in Figs. 5 and 6.

The perturbed-crystal eigenstates are solutions of

$$(1-gV)|\ \rangle=0, \tag{21}$$

which may be written as a set of N linear equations in the localized representation

$$\sum_m \{\delta_{n,m}-\langle n|gV|m\rangle\}\langle m|\ \rangle=0. \tag{22}$$

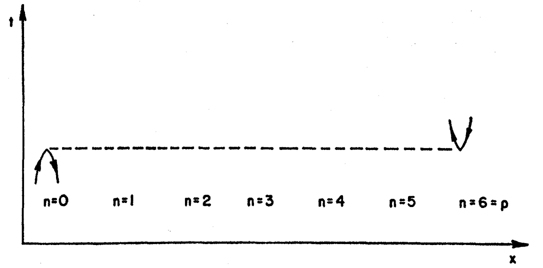

FIG. 5. Feynman diagram for the direct interaction between impurities. An upward (downward) directed line denotes an electron (hole); the dashed line represents the Coulomb interaction. The lattice points of the one-dimensional model are denoted by $n=0$, $1, \cdots, 6$, with the sensitizer at $n=0$ and the activator at $n=6\equiv p$.

Since V is a localized perturbation, there are only six sites, $m=A$, S, $A\pm1$, $S\pm1$, which enter the product matrix gV; thus, as long as we are interested in the impurity states and not in the perturbed host-exciton states, we may replace Eq. (22) with the set of six equations

$$\sum_m{}' A_{n,m}\langle m|\ \rangle=0, \tag{23}$$

where

$$A_{n,m}=\delta_{n,m}-\langle n|gV|m\rangle \tag{24}$$

and the prime on the summation restricts the sum to the six sites of interest. Thus the determination of the impurity eigenstates and eigenvalues has been reduced to the equivalent (but simpler) problem of finding the eigenvectors and eigenvalues of the localized matrix gV. The impurity energies which solve Eq. (23) are the roots of the 6×6 determinantal factor of Eq. (22)

$$\det A=0. \tag{25}$$

Since the perfect-crystal Hamiltonian is invariant under the symmetry operations of the space group, the Green's function is too. Hence, as a consequence of crystal periodicity and inversion symmetry, $\langle n|g|m\rangle$ is only a function of the distance between the two sites n and m. A straightforward calculation yields

$$\langle n|g|m\rangle\equiv g(|n-m|)=\frac{[x-(x^2-1)^{1/2}]^{n'}}{2\beta(x^2-1)^{1/2}}, \tag{26}$$

where $n'\equiv|n-m|$, $x\equiv(E-\alpha)/2\beta$, and we have as-

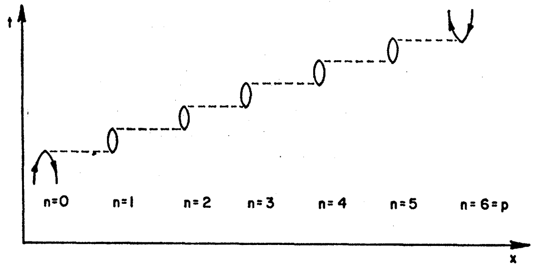

FIG. 6. Feynman diagram contributing to the indirect (virtual-exciton) interaction. A tightly bound localized excited state is denoted by a bubble.

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[32] Here we suppress the quantum number γ and assume that all relevant matrix elements are diagonal in it. The position of the nth lattice site is $R_n=na_L$, where a_L is the lattice constant.

sumed that E lies below the host-exciton band in the transparent region of the crystal ($x>1$). A further simplification of the problem results from the assumption that both impurities are identical, so that the determinantal eigenvalue equation (25) can be factored into parts corresponding to wave functions which are either odd or even under reflection through the plane midway between S and A; thus the impurity energies $E_\pm$ are determined by

$$\det[\mathbf{1}-(C_1\pm C_2)]=0, \tag{27}$$

where

$$C_1\pm C_2\equiv\begin{bmatrix} G_\pm(1) & H_\pm G_\pm(1)+G_\pm(0)+G_\pm(2) & G_\pm(1) \\ G_\pm(0) & H_\pm G_\pm(0)+G_\pm(-1)+G_\pm(1) & G_\pm(0) \\ G_\pm(-1) & H_\pm G_\pm(-1)+G_\pm(-2)+G_\pm(0) & G_\pm(-1) \end{bmatrix}, \tag{28}$$

$$H_\pm=(\delta\alpha\pm\Delta)/\delta\beta, \tag{29}$$

and

$$G_\pm(n)=\delta\beta[g(|n|)\pm g(|S-A|+n)]. \tag{30}$$

The resulting eigenvalue equations are

$$4(x_\pm^2-1)=2(x_\pm^2-1)^{1/2}(A+Dy_\pm^p+4y_\pm B\pm D\pm Ay_\pm^p \pm 2By_\pm^{p+1}\pm 2By_\pm^{p-1})+2B^2(1-y_\pm^2-y_\pm^{2p}) \pm B^2(y_\pm^{p-2}-2y_\pm^p-y_\pm^{p+2}), \tag{31}$$

where

$$A\equiv\delta\alpha/\beta,\quad B\equiv\delta\beta/\beta,\quad D\equiv\Delta/\beta,$$
$$y_\pm\equiv x_\pm-(x_\pm^2-1)^{1/2}<1,\quad\text{and}\quad p\equiv|S-A|. \tag{32}$$

[Recall $x_\pm\equiv(E_\pm-\alpha)/2\beta$.] Rather than become involved in unnecessarily tedious calculations, we set B equal to zero (nearest-neighbor coupling for impurity-host is the same as for host-host), with the understanding that we shall later generalize our results to the case $B\neq0$, using arguments based on perturbation theory. The simplified eigenvalue equation is

$$y_\pm^{-1}-y_\pm=A+Dy_\pm^p\pm D\pm Ay_\pm^p, \tag{33}$$

and the effective interaction is

$$\Delta_{\text{eff}}=\tfrac{1}{2}(E_+-E_-)\approx\tfrac{1}{2}\beta\delta y(1-y_-^{-2}), \tag{34}$$

where $\delta y\equiv y_+-y_-$ is sufficiently small to be treated as a differential and the minus subscript on y_- will henceforth be omitted. Thus we have[33]

$$\Delta_{\text{eff}}=\left[\frac{(1-y^2)}{1+y^2+(D+A)py^{p+1}}\right]\Delta+\left[\frac{(1-y^2)y^p}{1+y^2+(D+A)py^{p+1}}\right]\delta\alpha. \tag{35}$$

Since y is approximately equal to $\beta/\delta\alpha$, ($E\approx\alpha+\delta\alpha$), and is less than unity, the second term in the effective interaction decreases exponentially with the S-A separation $R=pa_L$, whereas the first term is proportional to the bare interaction Δ which is long-ranged (e.g., $\Delta\propto R^{-3}$). Therefore we write Δ_{eff} as a sum of long-ranged and short-ranged parts

$$\Delta_{\text{eff}}=\Delta_{\text{l.r.}}+\Delta_{\text{s.r.}}=\Delta/\epsilon+\Delta_{\text{s.r.}}, \tag{36}$$

the long-ranged part being tentatively identified as screened by the "dielectric constant" ϵ. [The quantity in brackets premultiplying Δ in Eq. (35) is ϵ^{-1}; note that the last term in the denominator of ϵ^{-1} represents "spatial dispersion."] In fact, both terms correspond to polarization processes which enter the (internal) inverse longitudinal dielectric operator defined by Hubbard.[34] It can be shown[35] that Hubbard's internal dielectric function is the same as the dielectric function measured by coupling a weak external longitudinal field to the many-particle system of interest—provided that the imaginary part of ϵ is small and local fields are negligible. The matrix element which enters the transition-rate Eq. (9) is Δ_{eff}, which for large impurity separations reduces to the form Δ/ϵ used in the FD theory; for smaller values of R, the short-ranged term[36] can seriously modify the radial dependence of the effective interaction, even providing the dominant contribution. Thus the FD resonance-transfer theory in its usual form is valid only for distances so large that $\Gamma\equiv|\Delta_{\text{s.r.}}/(\Delta/\epsilon)|\ll1$. This inequality is a semiquantitative statement of the earlier assertion that the FD theory is only valid if the

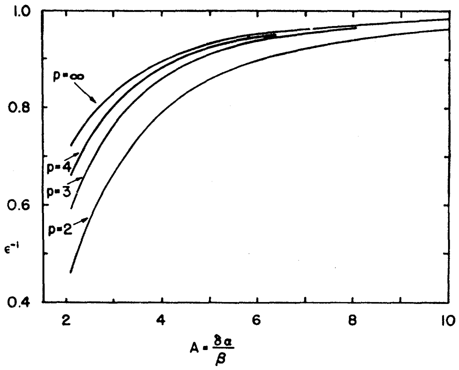

FIG. 7. The quantity ϵ^{-1} as a function of A [see Eqs. (35) and (36)].

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[33] This result reduces to Agranovich's (Ref. 25) for $\Delta=0$, $|\beta/\delta\alpha|\ll1$.

[34] J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957); **A243**, 336 (1958); **A244**, 199 (1958).

[35] A. Morita and Y. Osaka, Progr. Theoret. Phys. (Kyoto) **26**, 799 (1961).

[36] We emphasize that the short-ranged term is *not* due to exchange; since we assume that atomic wave functions on different sites do not overlap, the only way exchange could be incorporated into this model is by adding a spin-spin interaction term to the Hamiltonian.

impurities are sufficiently separated that their wave functions are essentially uncorrelated; we shall see that it is often a more restrictive weak-coupling condition than the usual requirement that $\hbar/\Delta$ be small compared with phonon equilibration times. The short-ranged term is due to indirect coupling between impurities by means of the virtual-exciton mechanism first discussed by Agranovich[25]; the virtual exciton hops from site to site until it arrives at the activator. Plots of ϵ^{-1} as a function of $A\equiv\delta\alpha/\beta$ are given for $p=2$, 3, 4, and ∞ in Fig. 7; likewise, $\xi\equiv-\ln y$, the inverse damping length per lattice constant for the short-ranged interaction, and y^p are plotted as functions of A for various values of p in Figs. 8 and 9. The short-range to long-range ratio Γ may be obtained by multiplying y^p by $(\beta+\delta\beta_0)(\beta+\delta\beta_p)\times(\delta\alpha)/(\beta^2\Delta)$; the factor $(\beta+\delta\beta_0)(\beta+\delta\beta_p)\beta^{-2}$ has been included to make the results reduce [in the limit $|(\delta\alpha)/\beta|\gg1$] to those obtained in lowest order of perturbation theory (the diagram of Fig. 5) for the case of non-identical S and A.

Of course, the virtual-exciton mechanism is intrinsically interesting and not just a troublesome process which interferes with the FD mechanism of energy transfer. Its range is typically about four lattice constants, as may be seen from the following numerical considerations. For interactions between nearest neighbors in realistic monatomic molecular crystals, the matrix element β is typically 0.1 eV, almost regardless of the multipolar nature of the interaction. For more distant neighbors, the bare direct matrix elements and critical transfer distances for dipole-dipole (*dd*), dipole-quadrupole (*dq*), quadrupole-dipole (*qd*), quadrupole-quadrupole (*qq*), and exchange (*ex*) are typically[37] (for inorganic systems)

$$\begin{aligned}&\Delta_{dd}\approx0.1p^{-3}\text{ eV}, && R_{dd}\approx35\text{ Å},\\ &\Delta_{dq}\approx0.02p^{-4}\text{ eV}, && R_{dq}\approx13\text{ Å},\quad R_{qd}\approx30\text{ Å},\\ &\Delta_{qq}\approx0.003p^{-5}\text{ eV}, && R_{qq}\approx15\text{ Å},\end{aligned}\tag{37}$$

and

$$\Delta_{\text{ex}}\approx10^3p^3e^{-2a_Lp/a_0}\text{ eV},\quad R_{\text{ex}}\approx5\text{ Å},$$

whereas the short-ranged interaction is typically (taking $a_L\approx6a_0$ and $|\delta\alpha|\approx2$ eV)

$$\Delta_{\text{s.r.}}\approx0.1(0.05)^{p-1}\text{ eV}.\tag{38}$$

Thus the virtual-exciton mechanism cannot compete with direct dipole-dipole transfer, but it will provide the dominant mechanism for *dq* and *qq* transitions over distances less than four and seven lattice spacings, respectively. Virtual-exciton transfer always dominates the long-ranged energy migration by the exchange mechanism.

These numbers indicate that for forbidden transitions, the conventional application of the FD theory to the interpretation of luminescence data may lead to erroneous results, especially when high concentrations of impurities are involved. In fact, virtual-exciton energy transfer may have been observed by a number of workers. For example, Nakazawa and Shionoya[38] have investigated transfer from Tb^{3+} to Nd^{3+} in calcium-metaphosphate glass, which they characterize as *dq* or *dq* transfer, not specifying which impurity has an allowed transition and which has a forbidden one. We believe that both transitions are forbidden and that virtual-exciton transfer is responsible for the observed energy migration. Likewise, the system[39] CaF_2(Ce,Mn)

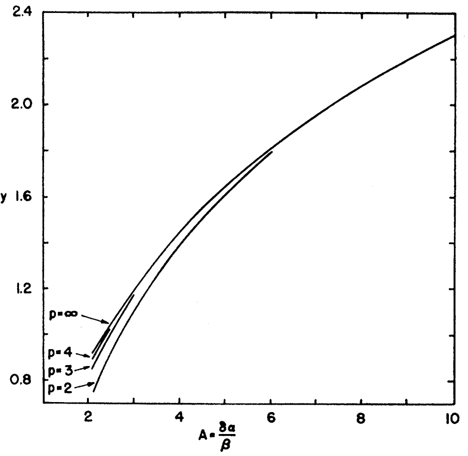

FIG. 8. $\xi=-\ln y$, the inverse damping length per lattice spacing, as a function of A.

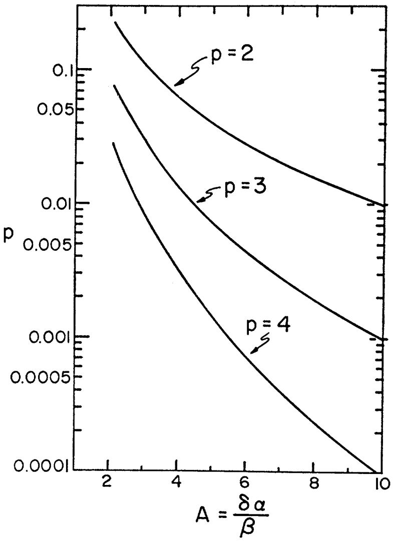

FIG. 9. y^p as a function of A.

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[37] Observe that $R_{qd}>R_{dq}$, since sensitizers with forbidden transition have longer radiative lifetimes.

[38] E. Nakazawa and S. Shionoya, Tech. Rept. Solid State Phys. University Tokyo A236, 1967 (unpublished); J. Chem. Phys. (to be published). We are grateful to Professor Nakazawa and Professor Shionoya for a copy of their paper.

[39] R. J. Ginther, J. Electrochem. Soc. **101**, 248 (1954); R. Leach, *ibid.* **105**, 27 (1958); B. L. Danielson, Phys. Rev. **142**, 228 (1966).

exhibits efficient spin-flip resonance transfer from Ce^{3+} to Mn^{2+} over distances of about 11 Å. This distance is probably a bit large for a direct exchange interaction, but not so large that virtual excitons ($\delta\alpha \sim 10$ eV) could not transfer the excitation in a two- or three-hop process.

A similar situation exists in organic systems. Smaller *et al.*,[40] assuming a phenanthrene-naphtahlene exchange transition rate[4] proportional to $\exp(-2R/L)$, obtained $L \approx 1.5$ Å, which they interpreted as an average Bohr radius or wave-function damping length. Calculations of the exchange integral for hydrogenic 1*s* orbitals show that the asymptotic behavior of the transition rate is more nearly $\sim(R/a_0)^6 \exp(-4R/a_0)$, where a_0 is the Bohr radius[41]; thus Dexter's L should be interpreted as *half* the average Bohr radius. A radius of 3 Å is unacceptably large (almost by a factor of 2), and we conclude that the virtual-exciton mechanism probably operates here too.

Finally, we note that Sternlicht, Niemann, and Robinson[42] have observed virtual-exciton migration by way of exchange interactions in deuterated benzene. Their basic technique is to vary $\delta\alpha$ by using heavy impurities. Similar techniques ought to be applied to the study of energy transfer in inorganic solids; depending on crystal symmetry, it should also be possible to change $\delta\alpha$ by applying a pressure to the crystal, possibly modulating it and observing the modulation of luminescence.

To be sure, we have only given a semiquantitative account of resonance transfer by virtual excitons in one dimension. It can be shown[28] that the three-dimensional analog of the model treated here has an asymptotic effective interaction of the Yukawa type, so that generalization to three dimensions does not result in significantly different results. Of course, the one-dimensional model is deficient in that it neglects (a) the effects of virtual-exciton hops between non-nearest neighbors, (b) higher-energy host bands, (c) multiple scattering in the case of several sensitizers or activators, and (d) scattering of the intermediate host-exciton states by phonons. Deficiency (a) can be removed by performing a numerical calculation of the effective interaction using a realistic Hamiltonian; the additional pathways for virtual-exciton migration will enhance this mechanism of energy transfer in one dimension and more so in three dimensions. The effects of higher-energy host bands must be included in order to have a consistent theory of energy transfer, since localized impurities necessarily couple strongly to high-energy states of the host. These states are often best described in terms of a basis set of atomic functions localized at the crystal-lattice sites, suitably symmetrized,[31] with *impurity* (rather than host) functions at the impurity sites; it is then convenient to define a pseudo-Hamiltonian which can be diagonalized by the exciton transformation in this basis.[15] Future attempts to extend the FD theory will doubtless concentrate on multiple-scattering effects and exciton-phonon interactions; the latter seem to be the sole threat to the virtual-exciton mechanism, since they may destroy the coherence of the intermediate states. It is our belief that for distances up to about five lattice spacings in typical strong-coupling host crystals (e.g., CdS[43]), the reduction of virtual-exciton migration by phonons is compensated for by the increased number of paths for that migration; thus our estimates of the strength of the indirect interaction, based on our simplified one-dimensional model, probably are about right for a realistic crystal.

It should be emphasized that the virtual-exciton mechanism described here is a *strong-coupling* version of a *net-weak-coupling* theory in the sense that nearest-neighbor interactions are strong (compared with phonon equilibration interactions), $\hbar/\beta \ll \tau_{\mathrm{eq}}$, while the net indirect and direct coupling is weak, $\hbar/\Delta_{\mathrm{eff}} \gg \tau_{\mathrm{eq}}$. Thus the crystal spectrum consists of relatively broad impurity bands lying below narrow host-exciton bands. The virtual-exciton mechanism certainly exists in crystals where the nearest-neighbor coupling is *intermediate* or *weak*, but its efficiency is attenuated by the exciton-phonon interaction.

IV. EFFECTIVE INTERACTION OF FD THEORY

In Sec. III, it was shown that the FD theory is valid only for energy transfer between widely separated impurities. We now turn to the problem of deriving the effective two-atom Hamiltonian for the FD theory from the full many-particle Hamiltonian of an idealized crystal. In spirit, the calculation is similar to the effective-mass theory for shallow donors in semiconductors as developed by Kohn and co-workers[44] and by others.[45] The underlying physical idea is that the effects of intervening charges on two spatially separated impurities should be primarily medium-like, allowing the intervening particles to be replaced with an electromagnetic field determined self-consistently and characterized by a frequency- and wave-number-dependent dielectric function. Using Kubo's theory of linear re-

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[40] B. Smaller, E. C. Avery, and J. R. Remko, J. Chem. Phys. **43**, 922 (1965)

[41] A factor $\exp(-4R/a_0)$, where a_0 is the average Bohr radius of the excited and unexcited states, will appear in the transition rate regardless of the details of the orbitals.

[42] H. Sternlicht, G. C. Nieman, and G. W. Robinson, J. Chem. Phys. **38**, 1326 (1963); G. C. Nieman and G. W. Robinson, *ibid.* **37**, 2150 (1962); **39**, 1296 (1963).

[43] The existence of an observable magneto-Stark effect [D. G. Thomas and J. J. Hopfield, Phys. Rev. Letters **5**, 505 (1960); Phys. Rev. **124**, 657 (1961)] in CdS indicates that at least the long-wavelength excitons have long mean-free-paths.

[44] W. Kohn, Phys. Rev. **105**, 509 (1957); **110**, 857 (1958); V. Ambegaokar, *ibid.* **121**, 91 (1961); L. J. Sham. *ibid.* **150**, 720 (1966).

[45] A. Morita, M. Azuma, and H. Nara, J. Phys. Soc. Japan **17**, 1570 (1962); Y. Abe, Y. Osaka, and A. Morita, *ibid.* **17**, 1576 (1962).

sponse[46] and the dielectric formulation of the many-body problem,[47] we show that in a suitable limit the bare interaction between two widely separated impurities is reduced by the same dielectric function which is measured optically, the relevant frequency being the energy of the transition divided by $\hbar$. Thus we provide a definite answer to the questions[10] concerning which dielectric function is to be inserted into the FD theory. Finally, we discuss local-field corrections and indicate to what extent they cancel in the usual FD theory.

In homogenous isotropic media, there are three relevant dielectric functions: (a) the square of the index of refraction, defined in terms of the polariton[48] dispersion relation

$$n^2(\mathbf{k},\omega)\equiv c^2k^2/\omega^2(\mathbf{k})\;; \tag{39}$$

(b) the longitudinal dielectric function ϵ_L relating the displacement to the longitudinal field

$$\mathbf{D}_L(\mathbf{k},\omega)=\epsilon_L(\mathbf{k},\omega)\mathbf{E}_L(\mathbf{k},\omega),\quad |\mathbf{k}\cdot\mathbf{E}_L|=|\mathbf{k}|\,|\mathbf{E}_L|\,; \tag{40}$$

and (c) the transverse dielectric function ϵ_T

$$\mathbf{D}_T(\mathbf{k},\omega)=\epsilon_T(\mathbf{k},\omega)\mathbf{E}_T(\mathbf{k},\omega),\quad \mathbf{k}\cdot\mathbf{E}_T=0\,. \tag{41}$$

For the case of inhomogeneous anisotropic media (e.g., noncubic crystals), these definitions become integral equations on $\mathbf{k}$ and the components of the dielectric tensor, e.g.,

$$\mathbf{D}_i(\mathbf{k},\omega)=\sum_{j=1}^{3}\int d^3\mathbf{k}'\,\epsilon_{ij}(\mathbf{k},\mathbf{k}',\omega)\mathbf{E}_j(\mathbf{k}',\omega)\,, \tag{42}$$

or, equivalently, in $\mathbf{r}$ space,

$$\mathbf{D}_i(\mathbf{r},t)=\sum_{j=1}^{3}\int d^3r'dt'\,\epsilon_{ij}(\mathbf{r},\mathbf{r}',\,t-t')\mathbf{E}_j(\mathbf{r}',t')\,. \tag{43}$$

The host dielectric function ϵ relates the displacement $\mathbf{D}$ to the total macroscopic field $\mathbf{E}$ in the crystal; in turn, $\mathbf{E}$ is a superposition of *external* plus *induced* (macroscopic) parts, the induced (longitudinal) field arising from the polarization charge density $\boldsymbol{\nabla}\cdot(\mathbf{E}-\mathbf{D})(1/4\pi)$. The quantity of immediate interest is χ, the response to just an *external* field. For transverse fields, ϵ_T is determined by the induced (coarse-grained) microscopic current and by Maxwell's equation (Ampere's law) for the displacement current:

$$\epsilon_T(\mathbf{k},\omega)=1+\frac{4\pi i}{\omega}\frac{\delta}{\delta\mathbf{E}_T(\mathbf{k},\omega)}\{\mathbf{J}_T(\mathbf{k},\omega)\}\equiv\chi_T(\mathbf{k},\omega)\,, \tag{44}$$

where the curly brackets denote averages over the host crystal's perturbed ground state and we assume homogeneity and isotropy of the host. For longitudinal fields, the induced charge density is

$$\begin{aligned}\{\rho(\mathbf{k},\omega)\}&=(4\pi)^{-1}[1-\epsilon_L(\mathbf{k},\omega)]i\mathbf{k}\cdot\mathbf{E}_L(\mathbf{k},\omega)\\&=(4\pi)^{-1}[1-\epsilon_L(\mathbf{k},\omega)]i\mathbf{k}\cdot[E_{\text{ext}}(\mathbf{k},\omega)\\&\qquad-i\mathbf{k}4\pi k^{-2}\{\rho(\mathbf{k},\omega)\}]\,,\end{aligned} \tag{45}$$

where we have neglected retardation of the Coulomb interaction. Thus the longitudinal dielectric function is defined by

$$\{\rho(\mathbf{k},\omega)\}=\frac{1-\epsilon_L(\mathbf{k},\omega)}{4\pi\epsilon_L(\mathbf{k},\omega)}i\mathbf{k}\cdot E_{\text{ext}}(\mathbf{k},\omega)\,, \tag{46}$$

which for a field due to a charge distribution, ρ_{ext} is equivalent to

$$\begin{aligned}\{\rho(\mathbf{k},\omega)\}&=[\epsilon_L^{-1}(\mathbf{k},\omega)-1]\rho_{\text{ext}}(\mathbf{k},\omega)\\&\equiv\chi_L(\mathbf{k},\omega)\rho_{\text{ext}}(\mathbf{k},\omega)\,.\end{aligned} \tag{47}$$

Physically, an isotropic crystal cannot distinguish between longitudinal and transverse fields which are spatially uniform; hence $\epsilon_L(0,\omega)=\epsilon_T(0,\omega)\equiv\epsilon(\omega)$. Mathematically, this result follows from the continuity equation applied to the longitudinal and transverse response functions.

From the theories of absorption and emission by single impurities,[23] we know that the transverse dielectric function evaluated at the photon wave-vector (i.e., effectively zero wave-vector) and the frequency of the transition enters in the determination of the multipolar matrix element in the FD theory; so does the index of refraction, which in the transparent region of interest is equal to $\epsilon^{1/2}(\omega)$. We shall see that the *longitudinal* dielectric function, evaluated at finite $\mathbf{k}$ and the transition frequency, enters into the effective impurity-impurity interaction. For dipole-dipole resonance transfer, in the absence of local-field corrections, the factors of $n(E)$ and $\epsilon(E)$ cancel, and the factor $\epsilon_L^{-2}(\mathbf{k},E)$ is the only dielectric function which remains in $R_{dd}{}^6$ [Eq. (4)]; for higher multipolar transfer, the transverse dielectric functions appear in the expressions for the critical transfer distances along with the factor $\epsilon_L^{-2}(\mathbf{k},E)$.

In what has preceded, we have restricted ourselves to isotropic media (e.g., cubic crystals) and have considered only the translationally invariant part of the response function

$$\epsilon(\mathbf{r},\mathbf{r}',t-t')\rightarrow\epsilon(\mathbf{r}-\mathbf{r}',\,t-t')\,, \tag{48}$$

in which case everything is most conveniently written in Fourier $(\mathbf{k},\omega)$ space. It is well known that the deviations from translational invariance are responsible for the so-called Lorenz-Lorentz local-field effects which generally depend on the detailed structure of the crystal in the region of the impurity.[22,23] For the case of a perfect static lattice,

$$\epsilon(\mathbf{k},\mathbf{k}',\omega)=\sum_{\mathbf{G}}\delta_{\mathbf{k}-\mathbf{k}'+\mathbf{G}}\,\epsilon(\mathbf{k},\mathbf{k}+\mathbf{G},\omega)\,, \tag{49}$$

where $\mathbf{G}$ is a reciprocal lattice vector. Adler has presented a general technique for solving the resulting

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[46] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[47] P. Nozières and D. Pines, Nuovo Cimento 9, 470 (1958).

[48] J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

integral equation in **G**, and in the dipole approximation he obtains the Lorenz-Lorentz formula modified by a self-polarization correction.[49] Wiser has considered the same problem from the viewpoint of self-consistent field theory, and has shown that the local field can be incorporated into a calculation *a posteriori* simply by performing a suitable average of the macroscopic field over a unit cell.[50] Even though the local-field correction depends on local-lattice deformation and whether the impurity occupies an interstitial or substitutional site, it is the same for single-impurity absorption and emission experiments as it is for resonance transfer between widely separated impurities. Therefore, as we have already indicated, all local-field effects cancel in the expressions for the FD critical transfer distances (provided that the remaining spatial dispersion in the longitudinal dielectric function can be neglected) and, for our purposes, may be neglected.

Turning now to the derivation of an effective impurity-impurity interaction, we write the Hamiltonian for a crystal plus two impurity atoms as a sum of (a) host-crystal Hamiltonian plus terms for the free impurities, (b) host-impurity interactions, and (c) impurity-impurity interactions:

$$H=H_a+H_b+H_c\,,$$

$$H_a=\sum_n T_n+T_S+T_A+\tfrac{1}{2}\rho_h\!:\!\rho_h+\tfrac{1}{2}\rho_i\!:\!\rho_i\,,$$

$$H_b=\rho_h\!:\!\rho_i\equiv\rho_h\!:\!\rho_A+\rho_h\!:\!\rho_S\,,$$

and

$$H_c=\rho_S\!:\!\rho_A\,, \tag{50}$$

where T_n is the kinetic-energy operator of the nth atom, ρ_h, ρ_S, and ρ_A are the charge-density operators for the host, the sensitizer, and the activator, respectively, and the scalar product denoted by a colon is defined by, e.g.,

$$\rho_h\!:\!\rho_A\equiv\int\!\!\int\frac{\rho_h(\mathbf{r})\rho_A(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'\,, \tag{51}$$

with the understanding that the interaction of a particle with itself is to be omitted. As in Sec. III, we recognize that the nuclear vibrations merely complicate the analysis in an unessential way, and we omit them. The strongest perturbation of the zero-order Hamiltonian H_a is the host-impurity coupling H_b; the inter-impurity coupling H_c is the very weak interaction responsible for the resonance energy transfer from S to A. We wish to eliminate the impurity-host interaction H_b and replace it with an effective impurity-impurity interaction involving the host dielectric function. In lowest order, we could simply average H over the unperturbed host ground state, but this procedure fails to account for the dielectric effects of the medium; thus it is desirable to recast the Hamiltonian in a form more suitable for studying the polarization of the host by the impurities.

Following Englert,[51] we perform a unitary transformation on H to remove the interaction H_b in lowest order:

$$\begin{aligned}\tilde{H}&=e^{-F}He^{F}\\&=H+[H,F]+\tfrac{1}{2}[[H,F],F]+\cdots\\&=H_a+H_b+H_c+[H_a,F]+[H_b,F]+[H_c,F]\\&\qquad+\tfrac{1}{2}[[H_a,F],F]+\cdots.\end{aligned} \tag{52}$$

The requirement that terms linear in H_b disappear determines F:

$$H_b+[H_a,F]=0\,, \tag{53}$$

so that, to lowest order, $\tilde{H}$ is given by

$$\tilde{H}=H_a+H_c+\tfrac{1}{2}[H_b,F]\,, \tag{54}$$

where

$$F=\frac{i}{\hbar}\int_0^\infty dt\,H_b(t) \tag{55}$$

and

$$H_b(t)=e^{iH_at/\hbar}H_be^{-iH_at/\hbar}. \tag{56}$$

Satisfactory unperturbed wave functions for the transformed Hamiltonian are products of host states and two impurity functions; that is, we neglect exchange between host and impurities. Averaging $\tilde{H}$ over the unperturbed host ground state provides us with an effective two-impurity Hamiltonian with an interaction term

$$\begin{aligned}H'=\rho_S\!:\!\rho_A&+\frac{i}{2\hbar}\int_0^\infty dt\,\rho_i(0)\!:\!\langle\rho_h(0)\rho_h(t)\rangle\!:\!\rho_i(t)\\&-\frac{i}{2\hbar}\int_0^\infty dt\,\rho_i(t)\!:\!\langle\rho_h(t)\rho_h(0)\rangle\!:\!\rho_i(0)\,,\end{aligned} \tag{57}$$

where the angular brackets denote host-ground-state averages. This already bears a resemblance to a bare interaction screened by a dielectric function, since ϵ is intimately related to the charge-density correlation function. Performing the time integrations and those implicit in the scalar products, and assuming translational invariance, we obtain the matrix elements of H' between unperturbed impurity states $|m)$:

$$\begin{aligned}(m|H'|n)=\sum_{\mathbf{q},\nu}&\frac{2\pi}{\Omega q^2}(m|\rho_i(\mathbf{q})|\nu)(\nu|\rho_i(-\mathbf{q})|n)\\&\times\{1-S_+[\mathbf{q},(E_\nu-E_n)/\hbar]+S_-[\mathbf{q},(E_m-E_\nu)/\hbar]\},\end{aligned} \tag{58}$$

where

$$S_\pm(\mathbf{q},\omega)=\frac{-4\pi i}{\hbar\Omega q^2}\int_{-\infty}^{\infty}\theta(t)\langle\rho_h(-\mathbf{q})\rho_h(\mathbf{q},\pm t)\rangle e^{i\omega t}dt\,, \tag{59}$$

Ω is the volume of the crystal, and $\theta(t)$ is the unit step function. The particular matrix element which enters

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[49] S. L. Adler, Phys. Rev. **126**, 413 (1962).

[50] N. Wiser, Phys. Rev. **129**, 62 (1963).

[51] F. Englert, J. Phys. Chem. Solids **11**, 78 (1959).

into the FD theory is $\langle a^*,s|H'|a,s^*\rangle$, so that the two possible intermediate states are $|\nu)=|a^*,s^*\rangle$ and $|\nu)=|a,s\rangle$. Thus we have

$$\langle a^*,s|H'|a,s^*\rangle=\sum_{\mathbf{q}}\frac{2\pi}{q^2}(a^*|\rho_A|a)(s|\rho_S(\mathbf{q})|s^*)$$
$$\times[2+S_+(-\mathbf{q},-E/\hbar)+S_+(\mathbf{q},E/\hbar)$$
$$-S_-(-\mathbf{q},E/\hbar)-S_-(\mathbf{q},-E/\hbar)], \quad (60)$$

where E is the transition energy [see Eq. (3)]. This may be compared with the longitudinal dielectric function obtained from the linear response of the host to an oscillating external charge distribution [Eq. (47)]

$$\epsilon_L^{-1}(\mathbf{k},\omega)-1=\frac{4\pi i}{\hbar\Omega k^2}\int_{-\infty}^{\infty}\theta(t)\langle[\rho(\mathbf{k},t),\rho(-\mathbf{k})]\rangle e^{i\omega t}dt$$
$$=S_-(-\mathbf{k},\omega)-S_+(\mathbf{k},\omega). \quad (61)$$

Substituting (61) into (60), invoking time-reversal symmetry of the host ground state, and realizing that causality implies that $\mathrm{Re}\,\epsilon_L^{-1}(\mathbf{k},\omega)$ is an even function of ω, while the imaginary part is odd, we have

$$\Delta_{\mathrm{eff}}\equiv\langle a^*,s|H'_{\mathrm{eff}}|a,s^*\rangle$$
$$=\sum_{\mathbf{q}}\langle a^*,s|H'_{\mathrm{bare}}(\mathbf{q})|a,s^*\rangle\,\mathrm{Re}\,\epsilon_L^{-1}(\mathbf{q},E), \quad (62)$$

where

$$H'_{\mathrm{bare}}(\mathbf{q})=(4\pi/\Omega q^2)\rho_A(\mathbf{q})\rho_S(-\mathbf{q}).$$

The traditional approximations used in the FD theory amount to neglect of spatial dispersion $\epsilon_L(\mathbf{q},E)\approx\epsilon_L(0,E)=\epsilon(E)$ and absorption $|\mathrm{Im}\,\epsilon(\mathbf{q},E)|\ll|\epsilon(\mathbf{q},E)|$. The first of these is valid only if the sensitizer and activator are distant from one another, as may be seen by spatially Fourier-transforming Eq. (62) to obtain a convolution of the inverse dielectric constant with the bare potential:

$$H'_{\mathrm{eff}}(E)=\int d^3\mathbf{r}d^3\mathbf{r}_1d^3\mathbf{r}_2\frac{\mathrm{Re}\,\epsilon_L^{-1}(\mathbf{r},E)\rho_A(\mathbf{r}_1)\rho_S(\mathbf{r}_2)}{|\mathbf{r}+\mathbf{r}_1-\mathbf{r}_2|}, \quad (63)$$

which, for dipole-dipole transfer, is

$$H'_{\mathrm{eff}}(E)=\int d^3\mathbf{r}\frac{\mathrm{Re}\,\epsilon_L^{-1}(\mathbf{r},E)}{|\mathbf{r}+\mathbf{R}|^3}$$
$$\times(\mathbf{M}_A\cdot\mathbf{M}_S-3\mathbf{M}_A\cdot\hat{R}\hat{R}\cdot\mathbf{M}_S). \quad (63')$$

Here we have assumed that $\epsilon_L^{-1}(\mathbf{r},E)$ is negligible except for those r much smaller than R. The convolution (63) can be trivially integrated if $\epsilon_L^{-1}(\mathbf{r},E)=\epsilon^{-1}(E)\delta(\mathbf{r})$, whereas $\epsilon_L^{-1}(\mathbf{r},E)$ is usually peaked near $r=0$ but has dispersion extending a few lattice spacings[52] [about as far as the range of the virtual-exciton mechanism; see Eq. (35)]. If the impurity separation R is large, the spatial dispersion has little effect on the value of the convolution integral, but for small R, it has a large effect. However, for such small values of R, linear-response theory becomes suspect, virtual excitons may be important, and it may not be possible to define an effective interaction in terms of a dynamically screened bare interaction; hence Eq. (63) is likely to be invalid. The requirement of negligible absorption at energy E [which allows us to replace $\mathrm{Re}\,\epsilon_L^{-1}$ with ϵ_L^{-1} in Eq. (63)] is usually fulfilled in low-impurity-concentration resonance-transfer experiments, since the hosts best suited for the study of transfer are transparent in the region of interest. At high impurity concentrations the "host" is really a dilute alloy and it is no longer correct to neglect "host" absorption. This is just another way of saying that multiple-scattering effects make the FD theory inapplicable to high-concentration systems.

V. SUMMARY

We have shown that the effective interaction of the FD theory may be written [Eq. (63)] as a bare interaction dynamically screened by a longitudinal dielectric function

$$H'_{\mathrm{eff}}(E)=[\epsilon^{-1}(E)]R^{-3}(\mathbf{M}_A\cdot\mathbf{M}_S-3\mathbf{M}_A\cdot\hat{R}\hat{R}\cdot\mathbf{M}_S) \quad (64)$$

for dipole-dipole transfer between impurities separated by several lattice constants [$R\gtrsim10a_L$] in a nondispersive [$\epsilon_L^{-1}(\mathbf{r},\omega)=\epsilon^{-1}(\omega)\delta(\mathbf{r})$], isotropic host medium (solid or liquid)[53] provided that local-field corrections are small. Hence the FD average dipole-dipole resonance transfer rate for an ensemble of single activators (A), distributed at random angles $\hat{R}$ with randomly oriented transition moments $\mathbf{M}_A$ a distance R from an excited sensitizer (S), may be written

$$\bar{P}_{SA}(dd)=(1/\tau_S)(R_{dd}^6/R^6), \quad (65)$$

where

$$R_{dd}^6\equiv\frac{9\hbar^4c^4}{8\pi}Q^0{}_A\int\frac{|\Phi_{dd}|^2}{\epsilon^2(E)}\frac{f_S(E)F_A(E)}{E^4}dE. \quad (66)$$

If spatial dispersion of the optical dielectric function is negligible, Eqs. (65) and (66) apply even though local-field effects may be large.

In addition to the usual weak-coupling criterion for each S-A pair, that the direct interaction Δ be much smaller than the overlap of impurity linewidths, it has

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[52] J. L. Fry, Ph.D. thesis, University of California at Riverside, 1966 (unpublished); H. Nara, J. Phys. Soc. Japan **20**, 778 (1965); **20**, 1097 (1965), and references therein; also Refs. 227–249 of Ref. 15.

[53] Although we have as yet made no reference to condensed media other than solids, for the most part the theory presented here applies equally well to dilute concentrations of impurities imbedded in disordered solids and liquids—provided that a_L is interpreted as an average lattice spacing. In the case of the virtual-exciton mechanism, a liquid host's Green's function is not diagonalized by the exciton transformation equation (14), but the mechanism still exists and can be evaluated in a localized-excitation picture by summing contributions to the migration rate from the various orders of perturbation theory.

been found that two further conditions must be satisfied for the FD theory to be applicable. First, virtual excitons must not provide an efficient transfer mechanism, $|\Gamma|\ll 1$, where

$$\Gamma\approx\frac{(\beta+\delta\beta_0)(\beta+\delta\beta_p)}{\beta\Delta}\left(\frac{\beta}{\delta\alpha}\right)^{R/a_L}, \tag{67}$$

β being the host-nearest-neighbor coupling, $(\beta+\delta\beta_0)$ and $(\beta+\delta\beta_p)$ being the coupling of sensitizer and activator, respectively, to the nearest host atom; $\delta\alpha$ is the energy difference between the lowest host-exciton band and the excited impurity level, R is the average impurity separation, and a_L is the lattice constant of the host. Second, it must be impossible, on the average, for two A's or two S's to be near enough to each other that one could provide a coherently coupled intermediate state influencing the rate of energy migration to or from the other. Both these requirements restrict the domain of validity of the FD theory to very low impurity concentrations. In this domain, the dependence of the transition rate on R can be unambiguously conconverted into a dependence on activator concentration, regardless of whether a particular S gives its energy to the nearest A or a more distant one. At high impurity concentrations (greater than 0.001, 0.1, 0.003, 0.03, and 1.0% for *dd*, *dq*, *qd*, *qq*, and *ex* transfer, respectively), the FD theory fails and multiple scattering must be taken into account. For transfer over short distances, the virtual-exciton mechanism often provides the dominant mechanism of energy transfer; it has been observed in energy transfer by exchange and may have been seen in multipolar-transfer experiments. Virtual-exciton energy transfer between inorganic impurities should be observable in hosts with weak exciton-phonon coupling. Virtual excitons are especially efficient for transferring energy when the impurities both have forbidden transitions, but one impurity may have an allowed transition and the mechanism will still be efficient for distances as large as four lattice spacings. The mechanism can be identified by monitoring sensitized luminescence intensity at fixed impurity concentrations as a function of $\delta\alpha$, the energy difference between the center of the lowest host-exciton band and the impurity states. Variation of $\delta\alpha$ can be accomplished by the isotopic means or by suitably modulating the pressure on the crystal.

The following extensions on the FD theory can and should be made: (a) inclusion of multiple-scattering effects; (b) investigation of the effects of exciton-phonon interactions on the virtual-exciton migration rate; (c) determination of corrections for medium anisotropy; (d) accounting for spatial dispersion in the local-field corrections; and (e) evaluation of the resonance transition rate for a realistic three-dimensional crystal with impurities. In all the cases but (a) and (b), improvement on the FD theory would require foregoing the advantages of measuring the transition matrix element and would demand calculation of correction terms. Thus the outstanding advantages of the theory in its present form would to some extent disappear.

Note added in proof. Since the preparation of this manuscript, White and Hogan have published an analysis of energy transfer by virtual excitons (via exchange coupling) in magnetic crystals [Phys. Rev. **167**, 480 (1968)].

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