

# PHYSICAL REVIEW LETTERS

VOLUME 33

30 SEPTEMBER 1974

NUMBER 14

## Theory of Fast and Slow Excitation Transfer Rates\*

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(Received 25 July 1974)

The two limiting cases of dipole-allowed excitation transfer rates between molecules,  $w \sim 1/R^3$  (Perrin) and  $w \sim 1/R^6$  (Förster), where  $R$  is the separation, may be obtained as well-defined limits of a single function  $w(R)$ . The demonstration is based on a model which allows the interaction strengths and relaxation rates to be compared explicitly and which has a generalization describing the situation in real molecules.

If a quantum mechanical system is placed in one of two degenerate states, each having a sharply defined energy and being coupled only to the other by an interaction matrix element  $u$ , the occupation probability oscillates between the two states at an angular frequency  $|u|/\hbar$ . One might define a "rate of transfer" as the reciprocal of the time required for the probability to build up to unity in the originally unoccupied state, or

$$w = 4|u|/\hbar, \quad (1)$$

where  $\hbar$  is Planck's constant ( $2\pi\hbar$ ). Equation (1) is often taken as the appropriate rate of "fast transfer" of electronic excitation between identical molecules, frequently via a dipole-dipole interaction  $u = \kappa\mu^2/R^3$ , where  $\kappa$  is a geometrical factor,  $\mu$  is the magnitude of the transition dipole moment, and  $R$  is the intermolecular separation. Between weakly interacting molecules the rate of excitation transfer is defined via an application of time-dependent perturbation theory as

$$w = 4\pi^2|u|^2/\hbar\Delta\epsilon, \quad (2)$$

where  $\Delta\epsilon$  is a factor roughly given by the spread in energy of the optical band associated with the transitions involved in the energy transfer.

Equations (1) and (2) or their equivalents are now a standard part of the large literature of ex-

citation transfer. There is an excellent review<sup>1</sup> by Förster, who first derived the explicit form of  $\Delta\epsilon$  in Eq. (2), and the conditions under which (1) and (2) apply were stated by Simpson and Peterson<sup>2</sup> and thoroughly analyzed by Robinson and Frosch.<sup>3</sup> Experimentally Eq. (2) or its equivalent has been confirmed in a wide variety of transfer experiments, for both like and unlike molecules, and for various interaction mechanisms.<sup>4</sup> While this is not true of Eq. (1) its strong coupling case is more naturally manifested in the appearance of a spectral splitting<sup>5</sup> proportional to  $|u|$ .

As derived, Eqs. (1) and (2) apply to a pair of molecules but they have been used extensively in qualitative discussions as hopping rates among systems of many molecules. The full description of probability flow in the analog of "fast transfer" in extended systems has been treated numerous times.<sup>6</sup> In the corresponding "slow-transfer" problem the rate (2) appears in the Pauli-type rate equations for the exciton motion, as first proposed by Förster<sup>7</sup> and elaborated upon by numerous authors.<sup>8</sup>

Recently descriptions of excitation transfer in extended systems have been developed in terms of density matrix equations and equations for the mean square displacement of the excitation,<sup>9-11</sup> but there has been no explicit quantitative connec-

tion made between Eqs. (1) and (2). In fact, since the derivations of Eqs. (1) and (2) are based on different definitions of the rate, it has been suggested<sup>12</sup> that they could probably never be compared in principle. An examination of the probability evolution for a pair of molecules shows that this suggestion is correct in a literal sense. If the evolution follows a Pauli-type rate equation [from which Eq. (2) is derived] the probability in the originally unoccupied state never builds up to unity and the definition leading to Eq. (1) becomes useless. Conversely the definition of  $w$  used in the "slow-transfer" case (the true rate of probability transfer at  $t=0$ ) predicts the equally useless result zero, when applied to the "fast-transfer" situation. A unique generalization of the two rate definitions is thus indeed impossible. However, we show here how the main contents of Eqs. (1) and (2) may be obtained as limiting cases of a *single* expression based on a *single* definition of the transfer rate. The theory also ascribes a width to the region in which the rate goes from the  $|u|$  to the  $|u|^2$  dependence ( $R^{-3}$  to  $R^{-6}$ , in the case of dipole interactions).

The first step in this demonstration is the redefinition of  $w$  in the more natural framework of exciton motion in a many-body, rather than a two-body, system. Consider, for simplicity, a linear chain of molecules with intermolecular spacing  $a$ . In terms of the mean square displacement  $\langle x^2 \rangle = \langle m^2 \rangle a^2 \equiv (\sum_m m^2 a^2 P_m) / \sum_m P_m$ , where  $P_m$  is the probability that the excitation is on molecule  $m$ , we define the rate  $w$  as the inverse of the time required for  $\langle x^2 \rangle$  to build up from 0 to the value  $a^2$ . An explicit equation<sup>13</sup> governing the evolution of  $\langle x^2 \rangle$  has been given by one of us. In the present context it yields

$$\frac{d\langle x^2 \rangle}{dt} = \langle A \rangle \int_0^t ds \varphi(s), \quad (3)$$

where

$$\langle A \rangle = [\sum_n P_n \sum_m F_{mn} (m-n)^2 a^2] / \sum_n P_n,$$

$F_{mn}$  are the transition probability rates, and  $\varphi(t)$  is the normalized "memory function" appearing in a non-Markoffian equation<sup>14</sup> for the probability evolution. The derivation of such an equation, a prescription for obtaining  $\varphi(t)$  from optical spectra, and the particular form of  $\varphi(t)$  for an actual system have been given earlier by the authors.<sup>11</sup> From Eq. (3), our definition of the rate  $w$  leads directly to

$$\langle A \rangle \int_0^{1/w} dt \int_0^t ds \varphi(s) = a^2. \quad (4)$$

Consider the further simplified model wherein the transfer matrix element is zero except between nearest neighbors and  $\varphi(t)$  is approximated by an exponential. In this case<sup>11</sup>

$$F_{mn} \varphi(t) = 2|u|^2 \hbar^{-2} e^{-\alpha t} (\delta_{m,n+1} + \delta_{m,n-1}), \quad (5)$$

and Eq. (4) yields for large systems ( $L \gg a$  where  $L$  is a measure of the system size) the following two particular results:

$$\frac{\alpha}{w} + e^{-\alpha/w} - 1 = \frac{\alpha^2 \hbar^2}{4|u|^2}, \quad (6)$$

$$\frac{\alpha}{w} + e^{-\alpha/w} - 1 = \frac{\alpha^2 \hbar^2}{2|u|^2}. \quad (7)$$

Equation (6) applies to the "two-sided" situation, i.e., one in which the distance of the molecule excited at  $t=0$  from either end of the chain is much larger than the intermolecular separation  $a$ , whereas Eq. (7) is obtained in the "one-sided" situation wherein the excitation is originally placed at one of the ends. The difference appears in the quantity  $\langle A \rangle$  which equals  $4a^2|u|^2/\alpha\hbar^2$  in the former but  $2a^2|u|^2/\alpha\hbar^2$  in the latter case. The two-body system involves an extreme size limit ( $L=a$ ) of the "one-sided" situation. In the respective limits  $\alpha \ll |u|/\hbar$  and  $\alpha \gg |u|/\hbar$ , Eq. (7) reduces to

$$w = 2\pi|u|/\hbar, \quad (1')$$

and

$$w = 8\pi^2|u|^2/\hbar^2\alpha. \quad (2')$$

Equation (2') is identical to (2) with the correspondence  $\alpha = 2\Delta\epsilon/\hbar$  and (1') differs from (1) only by the constant factor  $\pi/2$  which arises because of a peculiarity of the definition (1) and will be discussed below. The respective limiting values equal  $2\sqrt{2}\pi|u|/\hbar$  and  $16\pi^2|u|^2/\alpha\hbar^2$  for the large two-sided system.

Förster<sup>15</sup> compared Eqs. (1) and (2) for a typical case, choosing a spectral parameter  $\Delta\epsilon = 3000 \text{ cm}^{-1}$ . As shown above, this corresponds to a choice  $\alpha = 2\Delta\epsilon/\hbar = 1.799 \times 10^{14} \text{ sec}^{-1}$  in our memory function. In Fig. 1 we compare Förster's pairwise transfer rates<sup>16</sup> as a function of  $|u|$  (light curves) with the prediction of the present theory for an exponential memory [Eq. (7)] (heavy curve). Note that the latter coincides precisely with the light curve  $c$  in the " $R^{-6}$  region." Curves  $a$  and  $b$  are discussed below. The lower abscissa scale is essentially the Simpson-Petersen<sup>2</sup> parameter  $2|u|/\Delta\epsilon$ .

In the case of an exponential memory and a di-

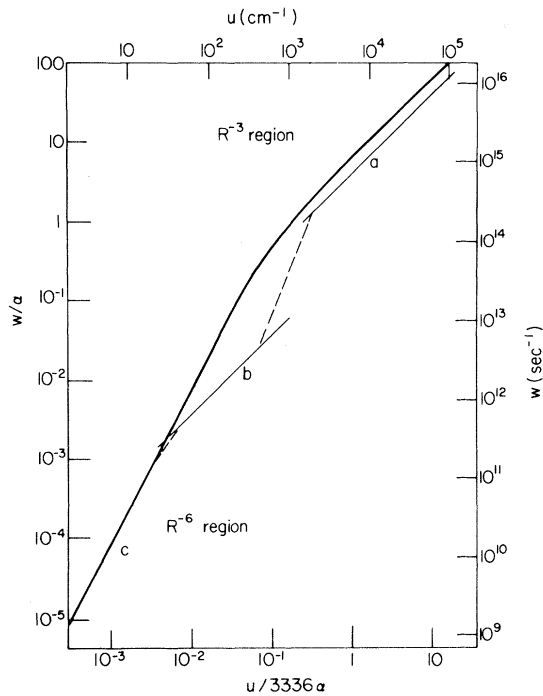


FIG. 1. Comparison of Förster's estimated rates (light curves and upper and right scales) and the single function predicted for an exponential memory (heavy curve and lower and left scales). Curves *a*, *b*, and *c* are Förster's "strong," "weak," and "very weak" coupling cases, respectively. Abscissa: *lower*,  $|u|/3336\alpha$  where  $u$  is in  $\text{cm}^{-1}$  and  $\alpha$  is in units of  $10^{14} \text{sec}^{-1}$ ; *upper*,  $|u|$  in  $\text{cm}^{-1}$ . Ordinate: *left*,  $w/\alpha$ , dimensionless; *right*,  $w$  in  $\text{sec}^{-1}$ . The dashed lines are the "intermediate cases" of Ref. 15, Fig. 3. We stress that the upper and right scales involve a particular choice  $\alpha = 1.8 \times 10^{14} \text{sec}^{-1}$ , chosen to correspond with Förster's value of  $3000 \text{cm}^{-1}$  for  $\Delta\epsilon$ .

polar interaction,  $u = (\text{const})R^{-3}$ , one may show that the exponent in the rate as a function of  $R$  ( $w \sim R^n$ ) is given by

$$n = \frac{d \ln w}{d \ln R} = 6 \left( \frac{w}{\alpha} - \frac{1}{1 - e^{-\alpha/w}} \right). \quad (8)$$

This function is shown in Fig. 2. It goes smoothly from  $-6$  (small  $w/\alpha$ ) to  $-3$  (large  $w/\alpha$ ) and one sees that if the exponent could be measured to within say,  $\pm 0.5$ , the transition would appear to occur within only one decade in the transfer rate. The result also shows that the term " $R^{-3}$  transfer" can only mean "fast transfer" if one means "fast relative to  $\alpha$ " and, conversely, " $R^{-6}$  transfer" can only mean "slow transfer" if one means "slow relative to  $\alpha$ ." The curve [Eq. (8), Fig. 2] is a universal function of  $w/\alpha$ , independent of the strength of the dipole-dipole interac-

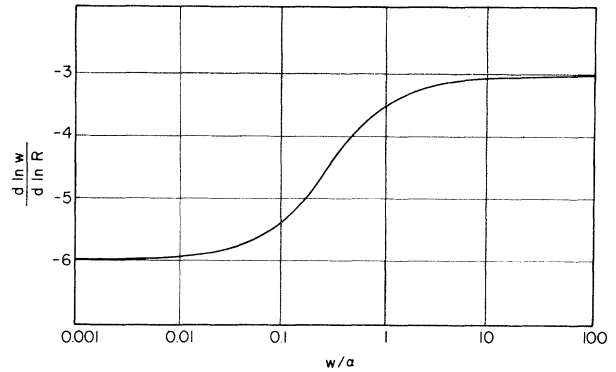


FIG. 2. The exponent of  $R$  in the transfer rate for the case of dipolar interaction, as a function of the transfer rate in units of  $\alpha$ . See text, Eq. (8). The inflection point is at  $w/\alpha \approx 0.22$ .

tion.

The fact that Eqs. (1) and (1') cannot be brought into complete accord, in contrast to the case of Eqs. (2) and (2'), is explained by the arbitrariness of the definition of the transfer rate in a two-molecule system. As we have remarked above, the probability in the originally unoccupied molecule never builds up to unity except in the purely coherent case and a smaller fraction must therefore be employed in a unified definition of the rate. The exact value of this fraction is arbitrary. The application of our large-system definition to the two-molecule system corresponds in the purely coherent case (fast transfer) to a parabolic approximation to the probability of excitation of the second molecule, while Eq. (1) defines the rate as the inverse of a quarter period of the true probability curve which is  $\sin^2(|u|t/\hbar)$ . This accounts for the factor  $\pi/2$  by which Eqs. (1) and (1') differ. In the two-molecule system there is a breakdown of the condition  $a \ll L$  satisfied in large systems. While our definition of the transfer rate is therefore not literally appropriate for the two-molecule system the difference shows up merely as a trivial constant factor of order unity. Factors of similar origin have been encountered earlier.<sup>3, 17</sup>

Förster's curve *b* (see Fig. 1) applies to his "weak" case in which  $R^{-3}$  transfer occurs as a result of strong overlapping of one vibronic absorption and emission band. As Gueron, Eisinger, and Schulman<sup>17</sup> have noted, this case is sufficiently different from curves *a* and *c* that it should not be compared with them directly. In the context of the present theory, if the molecules have complicated spectra and it is suspect-

ed that curve *b* might apply, one need only include a more detailed memory function as prescribed in Ref. 11. Generally, Eq. (4), rather than its particular form, Eq. (7), should be used, the curve analogous to the heavy curve in Fig. 1 being obtained by computing  $w = 1/f^{-1}(a^2/\langle A \rangle)$ , where *f* is the double integral in Eq. (4) taken as a function of the upper limit on the *t* integration.

As an example of the application of this formalism we choose the complex of five bacteriochlorophyll (BChl) molecules whose spectra have been studied in detail by Philipson and Sauer.<sup>18</sup> The low-temperature spectrum has a structure revealing an average pairwise interaction strength  $|u| \approx 125 \text{ cm}^{-1}$ . The value of  $\alpha$  estimated by using the BChl-*a* monomer spectrum at room temperature and assuming a Stokes shift comparable with that observed in bacteriopheophytin<sup>19</sup> is  $2.3 \times 10^{14} \text{ sec}^{-1}$  ( $\Delta\epsilon \approx 3800 \text{ cm}^{-1}$ ). Since  $|u|$  is essentially a dipolar interaction and is not expected to be temperature dependent, the above value of  $|u|$  persists so that  $|u|/3336\alpha$  at ordinary temperatures is 0.016. From Figs. 1 and 2 the transfer rate is found to be  $w \approx 0.020\alpha = 4.8 \times 10^{12} \text{ sec}^{-1}$  with an  $R^{-5.9}$  dependence. So, despite well-resolved splitting at low temperatures, the excitations in BChl complexes are not clearcut candidates for "fast" transfer at ordinary temperatures. Even if a two-sided transfer rate is more appropriate,  $w \approx 0.037\alpha$  with an  $R^{-5.8}$  dependence. This rough calculation suggests that fluorescence polarization measurements on the BChl-*a* complex may well reveal considerable depolarization, especially in view of the inference by Philipson and Sauer that the dipoles in the complex are not necessarily well ordered.

It is not completely clear how a direct measurement of the rates may be made over the whole range of  $|u|$ . However, we have now shown that one clear connection can be made between the two traditional limits and we are preparing an application of the theory to the time-dependence of fluorescence polarization in two-molecule systems.

The authors thank Professor D. L. Dexter for his comments and Vinita Ghosh for her assistance with computation.

\*Work supported in part by the National Science Foundation under Grant No. GU4040.

<sup>1</sup>Th. Förster, in *Modern Quantum Chemistry, Part III: Action of Light and Organic Molecules*, edited by O. Sinanoglu (Academic, New York, 1965), p. 93.

<sup>2</sup>W. T. Simpson and D. L. Peterson, *J. Chem. Phys.* **26**, 588 (1957).

<sup>3</sup>G. W. Robinson and R. P. Frosch, *J. Chem. Phys.* **37**, 1962 (1962), and **38**, 1187 (1963).

<sup>4</sup>L. Stryer and R. P. Haugland, *Proc. Nat. Acad. Sci. (U.S.)* **58**, 719 (1967) ( $R^{-6}$  transfer between unlike chromophores); R. S. Knox, *Physica (Utrecht)* **39**, 361 (1968) (review of polarization quenching by transfer in solution); L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, *J. Chem. Phys.* **45**, 1578 (1966) (higher-multipole transfer between rare-earth ions).

<sup>5</sup>A. S. Davydov, *Zh. Eksp. Theor. Fiz.* **18**, 210 (1948).

<sup>6</sup>E.g., R. E. Merrifield, *J. Chem. Phys.* **58**, 647 (1958); J. L. Magee and K. Funabashi, *J. Chem. Phys.* **34**, 1715 (1961).

<sup>7</sup>Th. Förster, *Ann. Phys. (Leipzig)* **2**, 55 (1948).

<sup>8</sup>D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953); M. Trlifaj, *Czech. J. Phys.* **8**, 510 (1958); P. Avakian, V. Ern, R. E. Merrifield, and A. Suna, *Phys. Rev.* **165**, 974 (1968).

<sup>9</sup>H. Haken and G. Strobl, in *The Triplet State*, edited by A. B. Zahlan (Cambridge Univ. Press, Cambridge, Mass., 1967), p. 311; M. K. Grover and R. Silbey, *J. Chem. Phys.* **54**, 4843 (1971); H. Haken and P. Reineker, *Z. Phys.* **249**, 253 (1972); S. Rackovsky and R. Silbey, *Molec. Phys.* **25**, 61 (1973); H. Haken and G. Strobl, *Z. Phys.* **262**, 135 (1973).

<sup>10</sup>V. M. Kenkre, *Phys. Lett.* **47A**, 119 (1974).

<sup>11</sup>V. M. Kenkre and R. S. Knox, *Phys. Rev. B* **9**, 5279 (1974).

<sup>12</sup>A. S. Davydov, *Phys. Status Solidi* **30**, 357 (1969); Förster, Ref. 1; see also D. L. Dexter and W. B. Fowler, *J. Chem. Phys.* **47**, 1379 (1967); G. Hoch and R. S. Knox, in *Photophysiology*, edited by A. Giese (Academic, New York, 1968), Vol. 3, p. 225; D. L. Dexter, Th. Förster, and R. S. Knox, *Phys. Status Solidi* **34**, K159 (1969).

<sup>13</sup>Ref. 10, Eq. (6).

<sup>14</sup>Ref. 11, Eq. (13).

<sup>15</sup>Th. Förster, in *Comparative Effects of Radiation*, edited by J. S. Kirby Smith and J. L. Magee (Wiley, New York, 1960), Chap. 13, p. 300.

<sup>16</sup>Ref. 15, Fig. XIII. 3.

<sup>17</sup>M. Gueron, J. Eisinger, and R. G. Schulman, *J. Chem. Phys.* **47**, 4077 (1967).

<sup>18</sup>K. D. Philipson and K. Sauer, *Biochemistry* **11**, 1880 (1972).

<sup>19</sup>J. C. Goedheer, in *The Chlorophylls*, edited by L. P. Vernon and G. R. Seely (Academic, New York, 1966), pp. 150–151.