Quantum theory of diffusion-accelerated remote transfer

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A theory of remote quenching of excited molecules in encounters with a quenching impurity is constructed which allows a consistent description of the course of the elementary energy-transfer event. The quenching rate constant for an (exchange) interaction that decreases exponentially with distance is computed. It is established that qualitative deviations from the contact model always occur not only in the case of too slow diffusion, but also in the case of rapid diffusion, when stochastic energy transfer is replaced by dynamic transfer, as manifested in the unusual hyperbolic decrease of the quenching rate with the growth of diffusion.

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1. INTRODUCTION

The migration of excited atoms and molecules facilitates their encounter with quenching impurity centers. The result of the encounter depends not only on how close the partners get and what interaction mechanism obtains, but also on how quickly the quenching zone is crossed. It is clear that the effectiveness w of the encounter should be a function of the diffusion coefficient D, which determines the duration of the encounter. However, the contact theory of luminescence quenching[1,2] either entirely ignores this circumstance (the "black" sphere model), or takes it into account in the most primitive manner, considering the quenching rate during the time of contact a constant (the "gray" sphere model). The more refined theory[3-5], which takes the extended nature of the interaction into account through the introduction of a local quenching probability U(r) that, by its very nature, cannot depend on D, is not free from this shortcoming.

At the same time, it is clear that the time of stay in the interaction zone, growing shorter with the speeding up of diffusion, can become less than the durations of those dissipative processes that ensure the very existence of the quenching probability. This indicates that a consistent computation of the encounter efficiency w should be based on an interaction Hamiltonian and mechanisms of energy relaxation, and not on the quenching probability. It is such a theory that is constructed in the present paper in the approximation of binary encounters of the excited particles with the quenching impurities. It is assumed that their interaction does not affect the interdiffusion process, i.e., that the coordinate measuring the distance between them is a parameter of the problem, and not a dynamical variable. It varies solely as a result of random walk, the mean migration in an elementary event being assumed to be small compared to the characteristic scale of the interaction. The last assumption is not absolutely necessary: if it is not fulfilled, we can develop an alternative hopping version of the theory similar to the one considered in[6]. However, we shall restrict ourselves in the present paper to the traditional successive-diffusion approach to the problem.

In the probabilistic formulation of the problem the basic tools are the kinetic equations[3]

$$\frac{dN(t)}{dt} = -k(t)CN(t) = -CN(t)\int U(r)n(r,t)dV, \tag{1.1}$$

$$\frac{\partial n(r,t)}{\partial t} = -U(r)n(r,t) + D\Delta n(r,t), \tag{1.2}$$

where N is the density of the excited donors in the sample, C is the concentration of the quenching impurity, and n(r, t) is the excitation density in the vicinity of a quencher, normalized to unity everywhere at the initial moment and at all times at points far from the quencher:

$$n(r,0) = n(\infty,t) = 1. \tag{1.3}$$

Such an approach to the problem allows a unified description of both static decay (D = 0), when an excitation decays at the location where it arises, and diffusion-accelerated quenching.

For any D quenching begins with static decay and ends with diffusion-assisted decay. When, however, a stable concentration profile $n_S = \lim_{t\to\infty} n(r,t)$ gets established around each acceptor, the complex kinetics of static and nonstationary quenching gives way to quasistationary exponential damping

$$N(t) = N(0)\exp(-kCt), \tag{1.4}$$

in which

$$k = \lim_{t\to\infty} k(t) = 4\pi D R_Q \tag{1.5}$$

has the meaning of a quenching-rate constant, R_Q being the effective radius of the quenching sphere.

In the "black" sphere model $R_Q = R = \text{const}$, while in the "grey" sphere model

$$R_Q = Rw = R\frac{k_p}{k_p + 4\pi RD} \tag{1.6}$$

is a two-parameter function of the diffusion coefficient, R being the radius of the interaction zone and k_p the quenching rate at the interaction-zone boundary: $4\pi R^2 n'(R) = k_p n(R)$. Owing to the increase in the number of parameters, the "grey" model is broader than the "black" model, but it too remains purely phenomenological, since it is impossible to relate R and k_p with the nature of the interaction and its extension in the framework of the contact theory. Furthermore, the form of the dependence $R_Q(D)$ is itself not always as in (1.6), even if U(r) is in fact different from zero only in the bounded region $r \le R$[7]. If, however, U(r) falls off smoothly with distance, then we can say what the dependence $R_Q(D)$ is only after the actual solution of the problem.

The refinement, proposed in the present paper, of the tools of the remote-transfer theory allows us to compute $R_Q(D)$ in those cases when the quenching has a probabilistic character, as well as in those cases when it is a dynamically developing—in the course of an

encounter—process. A concrete problem is solved for an (exchange) interaction that falls off exponentially with distance. It is established that qualitative deviations from the contact model occur both when the diffusion is very slow and when it is very rapid. Slowly migrating excitations die off at distant approaches to the quencher, so that the "black" sphere equivalent to it significantly exceeds it in dimensions. Furthermore, the radius of the sphere monotonically decreases with increasing D, not, however, according to a power law, as in (1.6), but logarithmically. The correspondence with the "grey" sphere model is attained only after R_Q, with the speeding up of the diffusion, comes close to R_0, the distance of closest approach of the particles, and only under the condition that the quenching occurs primarily in the thin contact layer. If, however, the encounters are so short that, while they last, the energy sink does not have time to discard the excitation energy, then their role amounts solely to the redistribution of the excitation, and the maximum efficiency decreases by a factor of two in comparison with the quenching "black" sphere: $w \leq 1/2$. Finally, when the duration of an encounter turns out to be shorter than all the relaxation times, the stochastic energy transfer mechanism is replaced by a dynamical mechanism, which manifests itself in a totally unusual hyperbolic decrease of the quenching rate with the growth of diffusion.

2. THE QUANTUM THEORY OF ENCOUNTERS

The kinetics of quenching and line broadening in liquid solutions can be considered from a standpoint analogous to the impact theory in gases if the mean distances between the particles in the donor-acceptor system are large enough for us to be able to limit ourselves to the consideration of their binary encounters. In this case it is not necessary to consider from the very beginning the quenching process to be stochastic and determine the probability of its occurrence over a distance r without allowance for the relative motion of the partners. There is no such limitation in the impact theory, and it should be eliminated in the encounter theory.

To achieve this, it is necessary to exclude the quenching probability from use by transforming (1.1) with the aid of (1.2):

$$\frac{dN}{dt} = -CN \int \left\{ D\Delta n(r,t) - \frac{\partial n(r,t)}{\partial t} \right\} dV. \qquad (2.1)$$

This refinement is adequate if the interval between the encounters is longer than the duration of their aftereffect. It is useful in the sense that it allows us to introduce in place of Eq. (1.2), an analog of a "master equation," an identical—in meaning—quantum equation for the density matrix

$$\dot{\rho}_{ik} = -\frac{i}{\hbar}[\hat{H}_0 + \hat{V}(r); \rho]_{ik} - P_{ik,lm}\rho_{lm} + D\Delta\rho_{ik}. \qquad (2.2)$$

The excitation density n(r, t) figuring in (2.1) is none other than the occupation number ρ_{11} of the term to be quenched. As to the boundary condition (1.3), it can be generalized in a natural way:

$$\rho_{ik}(r, 0) = \rho_{ik}(\infty, t) = \delta_{1i}\delta_{1k}. \qquad (2.3)$$

Besides the Hamiltonian $\hat{H}_0 + \hat{V}(r)$, which includes the interaction V(r) between the partners, we have introduced in (2.2) an intramolecular relaxation tensor P that takes into account the dissipation of the phases and the populations of the terms as a result of the interaction with the solvent and vacuum.

As in any microscopic theory, it is necessary for further progress to concretize the Hamiltonian and the dissipative properties of the system to correspond to some definite quenching mechanism. As an example, let us consider the quasiresonance, reversible energy transfer between two (and only two) terms 1 and 2 of the system (Fig. 1), a transfer which facilitates quenching because of the presence of a sink that empties the second term at a rate of $1/\tau$. This mechanism, which was proposed in[8], has been repeatedly tested in the static theory of energy transfer[9,10], and it is now necessary to establish what the modulation by the motion (through r(t)) of the interaction matrix element $b(r) = \langle 1 | \hat{V}(r) | 2 \rangle$ coupling the resonance terms leads to.

This interaction can have different origins. An impurity can act on the excited molecule as an external field, mixing the long-lived (1) and the short-lived (2) states, and thereby stimulating internal conversion in the course of an encounter. But there can also be a situation in which the excitation is captured by and deactivated on an impurity. Then the interaction couples, one to another, the collective states of the particle-impurity system, these states being characterized by the localization of the excitation. In the first case the aftereffect is negligible if the frequency of encounters of an excited molecule with impurity molecules is less than $1/\tau$, while on the other hand in the second case the aftereffect is negligible when the frequency of encounters of an impurity center with excitations does not exceed $1/\tau$. These conditions constitute supplementary restrictions on the impurity concentration in the first case and on the density of the excited states in second, but if they are satisfied, then the kinetic equation (2.1) is a good basis for the description of quenching, and the encounter efficiency is determined by the solution to a system of equations that are identical for both problems:

$$D\frac{1}{r}\frac{\partial^2}{\partial r^2} rn(r,t) + ib(r)\{\sigma(r,t) - \sigma^*(r,t)\} = \frac{\partial n(r,t)}{\partial t}, \qquad (2.4a)$$

$$D\frac{1}{r}\frac{\partial^2}{\partial r^2} rm(r,t) - ib(r)\{\sigma(r,t) - \sigma^*(r,t)\} - \frac{m(r,t)}{\tau} = \frac{\partial m(r,t)}{\partial t}, \qquad (2.4b)$$

$$D\frac{1}{r}\frac{\partial^2}{\partial r^2} r\sigma(r,t) - (\Gamma + i\omega_0)\sigma(r,t) + ib(r)\{n(r,t) - m(r,t)\} = \frac{\partial\sigma(r,t)}{\partial t}, \qquad (2.4c)$$

$$D\frac{1}{r}\frac{\partial^2}{\partial r^2} r\sigma^*(r,t) - (\Gamma - i\omega_0)\sigma^*(r,t) - ib(r)\{n(r,t) - m(r,t)\} = \frac{\partial\sigma^*(r,t)}{\partial t} \qquad (2.4d)$$

In these equations $n = \rho_{11}$, while $m = \rho_{22}$ and $\sigma = \rho_{12} = \rho_{21}^*$. The energy deficit is given by the parameter $\omega_0 = (E_1 - E_2)/\hbar$, while the quantity $\Gamma = \Gamma_1 + \Gamma_2$ is made up of the widths of the resonance terms. To the conditions identical with (2.3):

$$n(r, 0) = n(\infty, t) = 1, \quad m(r, 0) = m(\infty, t) = 0, \quad \sigma(r, 0) = \sigma(\infty, t) = 0, \qquad (2.5)$$

must be added one more boundary condition:

$$n'(R_0) = m'(R_0) = \sigma'(R_0) = 0, \qquad (2.6)$$

expressing the equality to zero of the particle flux when the particles are at their distance of closest approach

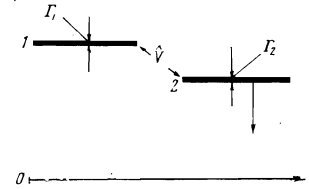

FIG. 1. Energy-level diagram of the donor-acceptor system. 1) the term being quenched, 2) the quenching term.

apart. Finally, in accord with the assumed interaction mechanism, we have

$$b(r)=b_0\exp(-\varkappa r). \tag{2.7}$$

The obtained kinetic equations allow us to investigate quasistationary (exponential) quenching, as well as nonstationary quenching, which is characterized by complex time kinetics. The latter is not of great interest to us here, since it is only partially connected with motion[1,2], it being in the other respects determined by the well-studied static quenching[11]. Furthermore, by restricting ourselves to quasistationary quenching, we can significantly simplify the problem by setting all the time derivatives in (2.4) and $\partial n/\partial t$ in (2.1) equal to zero. In such a case we immediately obtain from (2.1) the solution (1.4), i.e., an exponential decay proceeding at the rate given by (1.5). The only thing we need to compute in this case is the effective quenching radius R_Q, which, in view of the boundary conditions (2.6), is determined by only the asymptotic form of $n(r)$[12]:

$$R_Q=\frac{1}{4\pi}\int\Delta n\,dV=\int_0^\infty\frac{d}{dr}r^2\frac{d}{dr}n(r)\,dr=\lim_{r\to\infty}r^2\frac{dn}{dr}. \tag{2.8}$$

The asymptotic form of $n(r)$ is extremely simple:

$$n(r)\approx 1-R_Q/r. \tag{2.9}$$

Because of the boundary conditions (2.5), only one parameter remains in the asymptotic form, and this parameter is, as indicated by (2.8), R_Q.

Thus, the problem has been simplified and reduced to that of finding the asymptotic form of the steady-state solution of Eqs. (2.4). But even in such a formulation it is still fairly complicated. In order to facilitate matters, we shall consider successively three limiting situations differing in their time hierarchies:

$$\text{A)}\ 2\Gamma\geqslant\frac{1}{\tau}\gg\frac{1}{\tau_0},\quad \text{B)}\ 2\Gamma\gg\frac{1}{\tau_0}\gg\frac{1}{\tau},\quad \text{C)}\ \frac{1}{\tau_0}\geqslant 2\Gamma\gg\frac{1}{\tau}. \tag{2.10}$$

In any of them the interaction time τ_0 can be determined only a posteriori as a result of the solution of the system (2.4). It is certainly clear, however, that when this time is longer than the others, the diffusion terms in the last three equations of the system (2.4) can be neglected. In other words, in the situation A the variables σ, σ^*, and m attain their quasistationary values in such short times τ and Γ^{-1} that the distance between the partners does not have time to undergo any significant change as a result of diffusion. In the situation B this argument is applicable only to the variables σ and σ^*, whereas in Eq. (2.4b), in contrast, the diffusion term should be retained and the relaxation term dropped: there is not enough time for the decay to occur in the course of an encounter. Finally, in the situation C all the relaxation terms are small compared to the diffusion terms. When they are neglected, the system evolves strictly dynamically if we do not consider the random relative motion of the colliding partners, which acts in like manner on all the variables. All the three situations are distinguishable not only mathematically, but physically as well, which is underscored by the titles of the sections devoted to them.

3. LOCAL QUENCHING

Neglecting diffusion in all the equations of the system (2.4), except the first, we obtain from it by elimination of variables a single equation describing stationary quenching in the situation A:

$$D\frac{1}{r}\frac{d^2}{dr^2}rn(r)-W(r)n(r)=0, \tag{3.1}$$

$$n'(R_0)=0,\quad n(\infty)=1, \tag{3.1a}$$

which is characterized by the local probability

$$W(r)=\frac{U(r)}{1+U(r)\tau}. \tag{3.2}$$

the exact analog of the generalized probability of the static theory[8,10]. The quantity $W(r)$, being equal to the probability

$$U(r)=\frac{2b^2(r)\Gamma}{\omega_0^2+\Gamma^2}=U_0\exp(-2\varkappa r), \tag{3.3}$$

of energy transfer far from a quencher, becomes saturated and in the immediate vicinity of the quencher, where $U(r)$ exceeds the drainage rate $1/\tau$, it becomes equal to $1/\tau$. According to (2.7) and (3.3),

$$U_0=U(0)=\frac{2b_0^2\Gamma}{\omega_0^2+\Gamma^2},\quad U_m=U(R_0)=U_0\exp(-2\varkappa R_0). \tag{3.4}$$

If the saturation factor

$$Z=U_m\tau\ll 1. \tag{3.5}$$

then the draining of the energy is not shut off even in the case of continuity of partners, when the energy transfer proceeds at the maximum rate. In such a situation $W(r)=U(r)$ everywhere and the problem reduces to its probabilistic formulation (1.1)–(1.3), which ignores the possibility of saturation of the sink. However, upon the inversion of the inequality (3.5) the quenching probability $W(r)$ goes over into some similitude of the Fermi distribution (Fig. 2), and the difference between it and $U(r)$ in the vicinity of the quencher becomes significant. As $Z\to\infty$ and $\varkappa\to\infty$ ($Z^{1/\varkappa}=\text{inv}$), $W(r)$ degenerates into the rectangular function considered in[6,13,14] as a model of a strictly limited interaction. The base of the degenerate rectangle

$$R_z=R_0+\frac{1}{2\varkappa}\ln Z \tag{3.6}$$

establishes the radius of the region within whose boundaries quenching proceeds at the same rate equal to $1/\tau$ and outside of which no quenching takes place at all. Such a crude approximation of $W(r)$ is, however, not necessary, since the solution to the problem can be found in its general form. Indeed, according to the Appendix A, for any Z we have

$$R_Q=R_0+\frac{1}{2\varkappa}\left(\ln\gamma^2Z+2\psi(\nu)+\frac{1}{\nu}+2\pi\operatorname{ctg}\nu\pi\,\Lambda(Z,\xi,\nu)\right). \tag{3.7}$$

Here $\nu=(4\varkappa^2D\tau)^{-1/2}$, $\xi=\varkappa R_0$, $\gamma=\exp(C)$ (C is the Euler constant), $\psi(\nu)$ is Euler's psi function, while

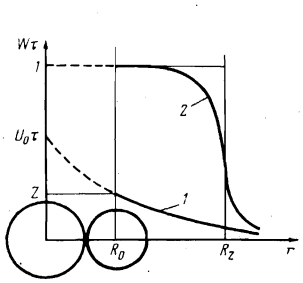

FIG. 2

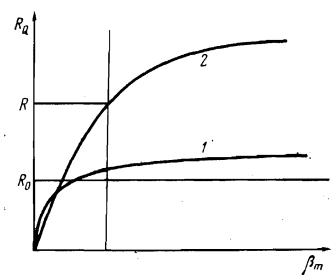

FIG. 3

FIG. 2. The coordinate dependence of the local quenching probability: 1) in the absence of saturation of the energy sink ($Z\ll 1$), 2) in the case of strong saturation of the energy sink ($Z\gg 1$).

FIG. 3. The behavior of the effective radius of the quenching sphere: 1) in the case of a thin quenching layer ($\xi\gg 1$), 2) in the case of an extended quenching layer ($\xi\ll 1$).

$$\Lambda(Z,\xi,\nu)=\frac{2\xi F'+Z(1-2\xi\nu)F}{2\xi(F'-e^{2i\pi\nu}\Phi')+Z(1-2\xi\nu)(F-e^{2i\pi\nu}\Phi)}, \qquad (3.7a)$$

where $F = F(\nu, \nu, 2\nu + 1; -1/Z)$ and $\Phi = \Phi(\nu, \nu, 2\nu + 1; -1/Z)$ are hypergeometric functions of the first and second kinds, respectively, and the primes indicate derivatives of the functions F and Φ with respect to their argument $-1/Z$.

Let us first turn to the situation when the inequality (3.5) is fulfilled and the sink is not saturated. Then, according to the Appendix A, the formula (3.7) can be transformed into the form

$$R_Q = R_0 + \frac{1}{2\varkappa}(\ln\gamma^2\beta_m + 2\Theta(\beta_m, 2\xi)), \qquad (3.8)$$

where the function $\Theta(x, y)$ is expressible in terms of the modified Bessel functions $I(2\sqrt{x})$ and $K(2\sqrt{x})$ and has the form

$$\Theta(x,y)=\frac{K_0(2\sqrt{x})-y\sqrt{x}K_1(2\sqrt{x})}{I_0(2\sqrt{x})+y\sqrt{x}I_1(2\sqrt{x})}. \qquad (3.8a)$$

The parameter $\beta_m = \nu^2 Z = U_m/4\varkappa^2 D$ or, in the general case, $\beta(r) = U(r)/4\varkappa^2 D$ is a local measure of quenching (the analog of action) determining the scale of the depletion, starting from the point r, of the excitation.

The behavior of the effective radius R_Q, (3.8), as a function of β_m is different for large and small values of this argument, i.e., in the regions respectively of slow and rapid diffusion (Fig. 3). These regions are delimited by that value of R_Q that corresponds to $\beta_m = 1$ (in Fig. 3, $\beta_m = 1$ is represented by the vertical straight line):

$$\begin{aligned} R_Q(1)=R&=R_0\left\{1+\frac{1}{\xi}\left(C+\frac{K_0(2)-2\xi K_1(2)}{I_0(2)+2\xi I_1(2)}\right)\right\}\\ &=R_0\left\{1+\frac{1.4+1.6\xi}{\xi(2.3+3.2\xi)}\right\}. \end{aligned} \qquad (3.9)$$

It is no coincidence that it is denoted in the same way as the radius of the quenching sphere in the contact model; when $R_Q(D)$ increases so much that it becomes comparable to R, the initially weak quenching becomes intense.

If the quenching is weak, i.e. if

$$\beta_m=\beta(R_0)\ll 1, \text{ and } R_Q\ll R, \qquad (3.10)$$

then in the expression for $\Theta(\beta_m, 2\xi)$, (3.8a), we can expand the cylindrical functions in series up to terms linear in β_m. Thus, we find a solution in which two particular cases

$$R_Q = R_0\frac{U_m\tau_e}{1+U_m\tau_e} \text{ for } \xi\gg 1, \qquad (3.11)$$

$$R_Q=\frac{U_m}{4\varkappa^2 D}(1+2\xi+2\xi^2) \text{ for } \xi\ll\frac{1}{\beta_m}, \qquad (3.12)$$

which overlap in the region $1 \ll \xi \ll 1/\beta_m$ ($\tau_e = R_0/2\kappa D$), can be distinguished. In the first case the radius R_0 of the sphere limiting the approach of the partners to each other is considerably larger than the thickness $1/\kappa$ of the adjoining quenching layer, while the opposite is true in the second case: $1/\kappa \gtrsim R_0$.

It is not difficult to verify that it is precisely the sphere with the thin quenching layer (and only it!) that is mathematically equivalent to the "grey" sphere specified in (1.6). In this case the radius R_0 of contact practically does not differ from the radius $R \approx R_0(1 + 1/\xi) \approx R_0$ of the quenching sphere, and the quenching rate at the boundary of the latter sphere, determined as a result of the identification of (1.6) with (3.11), is

$$k_p=\frac{2\pi R_0^2 U_m}{\varkappa}\approx\int_{R_0}^{\infty}U(r)4\pi r^2\,dr. \qquad (3.13)$$

Since it does not, in fact, depend on D, as was assumed in (1.6), the "grey" sphere model turns out to be quite acceptable, the phenomenological constant k_p finding a clear meaning of total probability of deactivation of donors uniformly distributed around the quencher. Here, as before, under the term "grey" sphere is meant its contact model, which, still within the limits of applicability of (1.6), not only does not rule out the possibility of the sphere becoming "black" with the slowing down of the diffusion, but, on the contrary, postulates it. It is precisely because of this that we compare it only with the solution (3.11), in which two stages are distinguishable: the kinetic stage, when $k_p/4\pi DR_0 = U_m\tau_e \ll 1$, $R_Q \ll R_0$, and the sphere is, in fact, "grey" in the sense of its efficiency ($w \ll 1$), and the diffusion-controlled stage, when $k_p/4\pi DR_0 = U_m\tau_e \gg 1$ and $R_Q \approx R_0$.

If, on the other hand, the extension of the quenching layer substantially exceeds R_0, then the quenching has little in common with the contact model. As can be seen from (3.12), the kinetic stage, i.e., the region of linear growth of $R_Q(\beta_m)$, is now not bounded by R_0, but extends far beyond the limits of the region of direct contact (Fig. 3) right up to $R_Q = R$.

Upon the inversion of the inequality (3.10), we have that the quenching near an acceptor is intense right up to the boundary whose radius is determined by the relation

$$\beta(R_S)=U(R_S)/4\varkappa^2 D=1. \qquad (3.14)$$

Since the boundary R_S has been moved far beyond the limits of the contact region ($R_S \gg R_0$), the contribution of the latter to the quenching efficiency is exponentially small: $\Theta \sim \exp(-4\sqrt{\beta_m})$. Neglecting this small quantity, we obtain from (3.8) the expression

$$R_Q=R_0+\frac{1}{2\varkappa}\ln\gamma^2\beta_m=\frac{1}{2\varkappa}\ln\frac{U_0}{4\varkappa^2 D}+\frac{1{,}15}{2\varkappa}. \qquad (3.15)$$

The dependence of R_Q on R_0, as on Θ, vanishes. This is understandable: all that happens deep inside the strong-interaction region loses importance as soon as the quenching is completely realized at the boundaries of the region. The validity of the last conclusion can be verified by a direct computation:

$$R_S=R_0+\frac{1}{2\varkappa}\ln\beta_m=\frac{1}{2\varkappa}\ln\frac{U_0}{4\varkappa^2 D} \qquad (3.16)$$

(see (3.14) and (3.3)). A comparison of (3.15) with (3.16) shows that the constantly maintained difference $\sim 1/\kappa$ between R_Q and R_S, which takes into account the partial destruction of the excitations beyond the limits of the strong-quenching region, is small and the slower the diffusion is, the less significant it is. This allows us in exchange quenching to regard R_S as an analog of the Weisskopf radius in the adiabatic theory of spectral-line broadening[8,15] [1)]. This radius for exchange quenching is sufficiently exactly determined by Eq. (3.14), which significantly differs from the corresponding relation given in[13]. Thus, the strong-quenching sphere is practically identical to the "black" sphere, whose radius increases logarithmically as the diffusion slows down (Fig. 3).

Let us now turn to the analysis of the situation in which the inequality (3.5) is inverted, so that strong saturation of the energy sink obtains. In this case we obtain from the general result (3.7) by expanding the hypergeometric functions in powers of $1/Z$ that

$$R_Q = R_0 + \frac{1}{2\varkappa}(\ln \gamma^2 Z + 2\psi(\nu+1) + \chi), \tag{3.17}$$

where

$$\chi = -\frac{1}{\nu}\left\{1 - 2\pi\nu\left[\operatorname{tg}\nu\pi - \nu\pi\left(\frac{1+2\nu\xi}{1-2\nu\xi}\right)\frac{\Gamma^2(2\nu+1)}{\Gamma^4(\nu+1)}Z^{2\nu}\right]^{-1}\right\}, \tag{3.17a}$$

and $\Gamma(2\nu + 1)$ and $\Gamma(\nu + 1)$ are the Euler gamma functions.

When $\nu^2 \gg 1$, the function χ is negligibly small, and, since $\psi(\nu + 1) \approx \ln \nu$ and $\beta_m = \nu^2 Z$, (3.17) reduces exactly to (3.15), i.e., for $\nu^2 \gg 1$ the result does not depend on whether or not there is saturation. This is easily explained. As is clear from (3.6) and the definition of $\beta(r)$, the quantity ν^2 is none other than $\beta(R_Z)$, and if $\nu^2 = \beta(R_Z) \gg 1$, then $\beta(r)$ is comparable to unity when $r = R_S \gg R_Z$. Consequently, the strong-interaction region, in the vicinity of whose borders the quenching is fully accomplished, is much more extended than the saturation zone lying inside it. Therefore, the presence or absence of this (saturation) zone does not affect the result.

The effect of the saturation of the sink can be manifested only in the $\nu^2 \ll 1$ case, when the diffusion is so fast that locally intense quenching is not attainable beyond the limits of the saturation zone: $R_S \ll R_Z$. But this means that it is, in general, unfeasible, since there obtains everywhere within the saturation zone spatially homogeneous quenching occurring at a rate of $1/\tau$. To obtain the result pertaining to this case, we should use the fact that ν is small, and, neglecting it in the arguments of the Euler functions, retain the first-order terms in the expansion of tan $\nu\pi$ in (3.17a). Thus, after simple transformations we obtain

$$R_Q = R_z - \frac{R_z - R_0}{\sqrt{\Delta}}\,\frac{\operatorname{sh}\sqrt{\Delta} + \mathcal{R}\operatorname{ch}\sqrt{\Delta}}{\operatorname{ch}\sqrt{\Delta} + \mathcal{R}\operatorname{sh}\sqrt{\Delta}}, \tag{3.18}$$

where

$$\Delta = \nu^2 \ln^2 Z = \frac{1}{\tau}\frac{(R_z - R_0)^2}{D}, \quad \mathcal{R} = \frac{\sqrt{\Delta}\,R_0}{R_z - R_0}. \tag{3.18a}$$

Like β_m, the quantity Δ has the meaning of action, but in the saturation zone—a spherical layer whose thickness $h = R_Z - R_0 = (2\kappa)^{-1} \ln Z$ is clearly greater than $\frac{1}{2}\kappa$. The coincidence of this result with the result obtained in[13,14] shows that the rectangle approximation to the coordinate dependence of $W(r)$ is admissible if $\nu^2 \ll 1$ or $\Delta \ll \ln^2 Z$. In the opposite case there obtains locally intense quenching described by the formula (3.15). As to the reducibility of the "rectangle model," (3.18), to the "grey" sphere model, (1.6), it is realizable only in the case of a narrow saturation zone: $R_Z - R_0 \ll R_0$ ($\xi \gg \ln Z$), although the numerical differences are not large at any ξ.

4. LOCAL TRANSFER

When the diffusion becomes so fast that there is no time for quenching to occur during an encounter, then the probability $W(r)$ of its occurrence per unit time also loses meaning. The only result of the encounters is now the transfer of energy to a metastable term that spontaneously empties itself in the intervals between the encounters. The transfer probability $U(r)$ is therefore the sole measure of the local effectiveness of the process in this situation. Indeed, after the neglect of the sink term m/τ in (2.4b) and the diffusion terms in (2.4c) and (2.4d) the system (2.4) reduces to two balance equations:

$$D\frac{1}{r}\frac{d^2}{dr^2}rn = -D\frac{1}{r}\frac{d^2}{dr^2}rm = U(r)(n-m), \tag{4.1}$$

which describe stationary transfer under the previous boundary conditions (2.5) and (2.6).

As shown in the Appendix C, a direct solution of (4.1) yields

$$2R_Q = R_0 + \frac{1}{2\varkappa}\{\ln 2\gamma^2\beta_m + 2\Theta(2\beta_m, 2\xi)\}. \tag{4.2}$$

It is not difficult to see that the right-hand side of this expression is obtainable from (3.8) by simply doubling β_m, owing to which the entire analysis of the behavior of (3.8) can be extended in a very simple manner to this situation. For weak transfer we obtain, instead of (3.11), the expression

$$R_Q = R_0 \frac{U_m\tau_e}{1+2U_m\tau_e} \text{ for } \xi \gg 1 \tag{4.3}$$

and exactly reproduce (3.12) for $\xi \ll 1$. If, on the other hand, the transfer becomes strong, then, instead of (3.15), we have

$$R_Q = \frac{1}{4\varkappa}\ln\frac{U_0}{4\varkappa^2 D} + \frac{1.84}{4\varkappa}. \tag{4.4}$$

Thus, differences appear only in the case of strong transfer, and amount, roughly speaking, to this that the radius of the "black" sphere decreases by a factor of two as a result of the saturation of the energy sink. This is natural; in the case of strong transfer the excitation is equally divided during an encounter between the two terms, but only that half of the excitation that appears in the state 2 decays.

5. NONLOCAL TRANSFER

All the solutions given above become invalid when diffusion interrupts an encounter before phase relaxation is able to develop. In such a situation—under the conditions (2.10 C)—not only the quenching probability, but also the transfer probability per unit time, loses meaning. The transfer develops during an encounter not stochastically, but dynamically; therefore, only the final result can be estimated, i.e., the result of an encounter can be estimated only after the entire encounter has taken place, and not at the various stages of the approach of the partners to each other. Dropping all the dissipative terms in (2.4), and neglecting nonresonance transfer, we obtain the system of equations

$$D\frac{1}{r}\frac{d^2}{dr^2}rn = -D\frac{1}{r}\frac{d^2}{dr^2}rm = -ib(r)(\sigma - \sigma^*), \tag{5.1a}$$

$$D\frac{1}{r}\frac{d^2}{dr^2}r\sigma = -D\frac{1}{r}\frac{d^2}{dr^2}r\sigma^* = -ib(r)(n-m), \tag{5.1b}$$

in which the sole local characteristic is the interaction itself, which attains at the maximum (at the time of contact) the value $b_m = b(R_0)$.

The solution of the problem has, according to the Appendix C, the form

$$2R_Q = R_0 + \frac{1}{\varkappa}(\ln 2\gamma^2\alpha_m + 2\operatorname{Re}\Theta(2i\alpha_m, \xi)). \tag{5.2}$$

The quantity $\alpha(r) = b(r)/\kappa^2 D$ is a true action, the analog of $\beta(r)$ in the preceding situations, and $\alpha_m = b_m/\kappa^2 D$ is its maximum value, which establishes the boundary between the weak and strong nonlocal transfer: $\alpha_m = 1$. At this boundary

$$2R_Q(1) = 2R \approx R_0\left[1 + \frac{1}{\xi}\ln 2\gamma^2\right]. \tag{5.3}$$

For $\alpha_m \ll 1$ there obtains weak transfer: $R_Q \ll R$, while for $\alpha_m \gg 1$ we have strong transfer: $R_Q \gg R$.

For weak nonlocal transfer expansion in powers of $\alpha_m \ll 1$ is admissible and yields

$$R_Q = R_0 \frac{4b_m^2\tau_e^2}{1+8b_m^2\tau_e^2} \quad \text{for } \xi \gg 1, \qquad (5.4a)$$

$$R_Q = \frac{b_m^2}{2\varkappa^5 D^2}\{5+10\xi+10\xi^2+4\xi^3\} \quad \text{for } \xi \ll 1. \qquad (5.4b)$$

At the diffusion-controlled stage the sphere with a thin quenching layer becomes almost "black," i.e., its efficiency ceases to depend on diffusion, but, for the same reasons as in the preceding situation, it attains in the limit not 1, but ½. In the kinetic phase, however, the solutions (5.4) differ markedly from the previously obtained solutions, independent of the thickness of the layer. The effective radius in this phase increases with 1/D not linearly, but quadratically, and, accordingly, the quenching rate is not constant, as is usually the case, but increases linearly as the diffusion slows down: $k = 4\pi D R_Q \sim 1/D$. This distinctive feature is characteristic of reactions that proceed dynamically under conditions of weak interaction, and is a diffusion analog of the Born approximation in the theory of collisions[16].

In the case of strong transfer, we can, by using the asymptotic forms of I and K for $\alpha_m \gg 1$, easily verify that $\Theta \sim \exp(-4\alpha_m)$ and, neglecting this small quantity, that

$$2R_Q = R_0 + \frac{1}{\varkappa}\ln 2\gamma^2\alpha_m = \frac{1}{\varkappa}\ln 2\gamma^2\frac{b_0}{\varkappa^2 D}. \qquad (5.5)$$

Strong transfer in this case is effected by the similitude of a "black" sphere whose efficiency is less than the usual efficiency by a factor of two because of saturation, while the radius logarithmically increases as before with increasing 1/D. The general idea about the function $R_Q(D)$ in the situation C (see Sec. 2) yields Fig. 3 if α_m^2 is plotted along the abscissa instead of β_m. However, the contrast between this situation and the others and the distinctive feature characteristic of it in the kinetic phase are better discerned from the dependence $k(1/D)$ (Fig. 4). Resonance nonlocal transfer is easily recognized by the linear growth of $k(1/D)$ in the case of rapid diffusion. With the slowing down of the diffusion the process reaches the usual kinetic stage ($k = \text{const}$) (the continuous curve in Fig. 4), but it is possible for the nonlocal transfer to give way to local transfer or quenching even when the sphere is "black" and K decreases with increasing 1/D (the dashed line in Fig. 4). As can be seen from the figure, the "grey" sphere model is inadmissible in both the case of rapid diffusion (in the dynamical phase) and the case of too slow diffusion (in the strong-interaction region).

APPENDIX A

Equation (3.1) with the variable r replaced by x:

$$r = R_0 + \frac{1}{2\varkappa}\ln(-xZ), \quad -\infty < x \leqslant -\frac{1}{Z} < 0 \qquad (1)$$

and the sought function $n(r(x))$ by $w(x)$:

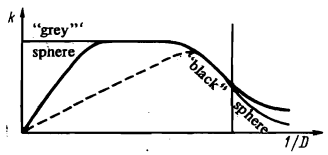

FIG. 4. Dependence of the quenching-rate constant on diffusion (the vertical boundary separates the regions of strong and weak interaction).

$$w(x) = n(r(x))r(x)x^{-\nu} \qquad (2)$$

reduces to Gauss's hypergeometric equation

$$x(1-x)w'' + (2\nu+1)(1-x)w' - \nu^2 w = 0, \qquad (3)$$

which has the general solution:

$$w(x) = a_1 F(\nu, \nu, 2\nu+1, x) + a_2 e^{2i\pi\nu}\Phi(\nu, \nu, 2\nu+1; x). \qquad (4)$$

Using the boundary conditions on the function $w(x)$ that follow from (2) and (3.1a):

$$2\xi w'\left(-\frac{1}{Z}\right) = Z(2\xi\nu-1)w\left(-\frac{1}{Z}\right), \qquad w(x) \sim x^{-\nu}\frac{1}{2\varkappa}\ln(-x), \quad x \to -\infty \qquad (5)$$

and the formulas giving the asymptotic expansions of F and Φ[17,18], we obtain

$$a_1 = \frac{1}{2\varkappa q}[1-\Lambda(Z,\xi,\nu)], \quad a_2 = \frac{1}{2\varkappa q}\Lambda(Z,\xi,\nu), \qquad (6)$$

where $q = 2\Gamma(2\nu)\exp(-i\pi\nu)/\Gamma^2(\nu)$ and $\Lambda(Z, \xi, \nu)$ is determined by the formula (3.7a). Using (2) and (4), we establish that the coefficient R_Q of the asymptotic expansion of $n(r)$ for $r \to \infty$ is connected with a_1 and a_2 by the relation

$$R_Q = R_0 + \frac{1}{2\varkappa}\ln Z + q\left\{2a_2\pi\operatorname{ctg}\nu\pi + (a_1+a_2)\left(2C + 2\psi(\nu) + \frac{1}{\nu}\right)\right\}, \qquad (7)$$

from which we obtain the required result (3.7) with the aid of (6).

The expression (3.7) for $Z \ll 1$ can be reduced to (3.8) with the aid of the following formulas, which are valid for $Z \to 0$, $\nu \to \infty$, and $\nu^2 Z = \beta_m = \text{const}$:

$$\begin{aligned} &F(\nu, \nu, 2\nu+1; -1/Z) \sim K_0(2\sqrt{\beta_m}); \quad \psi(\nu) \sim \ln\nu, \\ &\Phi(\nu, \nu, 2\nu+1; -1/Z) \sim e^{-2i\pi\nu}\{K_0(2\sqrt{\beta_m}) - \pi\operatorname{ctg}\nu\pi I_0(2\sqrt{\beta_m})\}, \\ &F'(\nu, \nu, 2\nu+1; -1/Z) \sim \nu Z\{K_0(2\sqrt{\beta_m}) - \sqrt{Z}K_1(2\sqrt{\beta_m})\}. \\ &\Phi'(\nu, \nu, 2\nu+1; -1/Z) \sim \nu Z e^{-2i\pi\nu}\{[K_0(2\sqrt{\beta_m}) \\ &-\sqrt{Z}K_1(2\sqrt{\beta_m})] - \pi\operatorname{ctg}\nu\pi[I_0(2\sqrt{\beta_m}) + \sqrt{Z}I_1(2\sqrt{\beta_m})]\}. \end{aligned} \qquad (8)$$

APPENDIX B

Setting the sought functions

$$n = (\xi+\eta)/2r, \quad m = (\eta-\xi)/2r, \qquad (9)$$

we transform the system of equations (4.1) into the form

$$\frac{d^2}{dr^2}\eta = 0, \quad \frac{d^2}{dr^2}\xi - 8\varkappa^2\exp[2\varkappa(R_0-r)]\xi = 0, \qquad R_0\eta'(R_0) = \eta(R_0), \quad R_0\xi'(R_0) = \xi(R_0), \quad \eta \sim \xi \sim r \ (r \to \infty). \qquad (10)$$

The solution to the first equation in (10) is $\eta = r$; the solution to the second can be found with the aid of the replacement of the variable r by x: $r = R_0 - \kappa^{-1}\ln x$, reducing it to the modified Bessel equation:

$$\xi'' + \frac{1}{x}\xi' - 8\beta_m\xi = 0, \qquad \xi\xi' + \xi|_{x=1} = 0, \quad \xi \sim -\frac{1}{\varkappa}\ln x \ (x \to 0), \qquad (11)$$

which has the general solution

$$\xi = a_1 I_0(2\sqrt{2\beta_m}\,x) + a_2 K_0(2\sqrt{2\beta_m}\,x). \qquad (12)$$

Using the boundary conditions, we find that

$$a_1 = -\frac{1}{\varkappa}\Theta(2\beta_m, 2\xi), \quad a_2 = \frac{1}{\varkappa}, \qquad (13)$$

where $\Theta(x, y)$ is given by the formula (3.8a). With the aid of (9) we establish that

$$R_Q = \tfrac{1}{2}(R_0 + a_2\ln\gamma\sqrt{2\beta_m} - a_1), \qquad (14)$$

from which after substituting for a_1 and a_2 from (13) we obtain the result (4.2).

APPENDIX C

Introducing the new unknown functions

$$\eta=r(n+m), \quad \varepsilon=r(n-m+\sigma-\sigma'), \quad \zeta=r(n-m-\sigma+\sigma'), \tag{15}$$

we can reduce the system of equations (5.1) to the closed system of three equations:

$$\frac{d^2}{dr^2}\eta=0, \quad \frac{d^2}{dr^2}\varepsilon+2i\varkappa^2\alpha_m\exp[\varkappa(R_0-r)]\varepsilon=0,$$
$$\frac{d^2}{dr^2}\zeta-2i\varkappa^2\alpha_m\exp[\varkappa(R_0-r)]\zeta=0. \tag{16}$$

In this case the function n necessary for the computation of R_Q is uniquely expressible in terms of η, ϵ, and ζ. Taking into account the fact that from a comparison of the last two equations in (16) follows the relation $\epsilon = \zeta^*$, we obtain for n the expression

$$n=\frac{1}{2r}\left(\frac{\varepsilon+\zeta}{2}+\eta\right)=\frac{1}{2r}\mathrm{Re}(\zeta+\eta), \tag{17}$$

which differs from the analogous expression for n given in (9) in that the real part is taken here. Since the equations in (16) for the quantities η and ζ differ from the system (10) only by the replacement of 2κ by κ (2ξ by ξ) and β_m by $i\alpha_m$, to find R_Q in the situation under consideration, it is sufficient to use the result (4.2), replacing in it 2κ by κ (2ξ by ξ) and β_m by $i\alpha_m$, and then taking the real part. As a result, we obtain (5.2).

[1)]The Weisskopf radius establishes a boundary in the immediate vicinity of which a complete reduction of the phase occurs, whereas practically nothing happens beyond this boundary, nor is there anything to add to what happens near the boundary when we move from the boundary into the region defined by it.

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