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Singlet and Triplet Products of the Geminate Recombination of a Radical Pair with a Single Magnetic Nucleus ($I = 1/2$)

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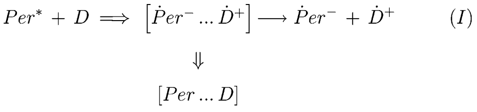
The double-channel recombination and separation of the photochemically created singlet radical pair is investigated, taking into account the spin conversion in a zero magnetic field and the arbitrary initial distance between the radicals. The quantum yields of the singlet and triplet products and the free radicals production are found analytically, assuming that the recombination of the diffusing radicals occurs at contact. All the yields are related to the singlet and triplet populations of the recombining radical pair, subjected to spin conversion and contact exchange interaction. The general analytical expressions for the quantum yields are specified for the particular limits of the weak and strong exchange. They are greatly simplified in the case of polar solvents, especially at the contact start. A close similarity is obtained with the results of a previously developed incoherent model of spin conversion, provided that the conversion rate is appropriately related to the hyperfine coupling constant.

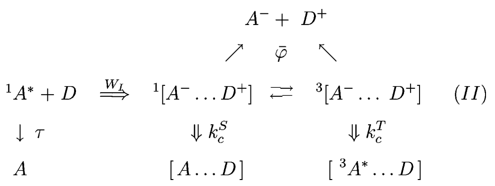
I. Introduction

The singlet radical-ion pair (RIP) created by photoinduced forward electron transfer is subjected to spin conversion, which populates its triplet state as well. The backward electron transfer in the singlet RIPs proceeds into the ground state of the neutral products (or into the nearest excited singlet), while the triplet RIPs recombine into their excited triplet state. The appearance of the triplet excitation as a consequence of geminate RIP recombination was first detected in the classical works of Weller at al.[1,2] and explained semiquantitatively by Schulten and Schulten.[3] In their pioneering work, the rates of recombination through the singlet and triplet channels were assumed to be equal, so that the recombination was “spin independent”. The presence of the triplet recombination channel in line with a singlet one was indirectly confirmed by the theoretical interpretation of Mataga’s data on the kinetics of the accumulation and separation of RIPs.[4] Later on, the triplets were experimentally determined in the very same system in which excited perylene (Per) was quenched by some aromatic amines (D):



$$\begin{array}{cccccc} Per^* + D & \Longrightarrow & \left[\dot{P}er^- \ldots \dot{D}^+\right] & \longrightarrow & \dot{P}er^- + \dot{D}^+ & (I) \\ & & \Downarrow & & & \\ & & [Per \ldots D] & & & \end{array}$$

To discriminate between the parallel singlet and triplet recombination channels, this spinless reaction scheme was substituted by the following comprehensive analog:[5]



$$\begin{array}{cccccc} & & & A^- + D^+ & & \\ & & \nearrow & \bar{\varphi} & \nwarrow & \\ {}^1A^* + D & \xRightarrow{W_I} & {}^1[A^- \ldots D^+] & \rightleftarrows & {}^3[A^- \ldots D^+] & (II) \\ \downarrow \tau & & \Downarrow k_c^S & & \Downarrow k_c^T & \\ A & & [A \ldots D] & & [{}^3A^* \ldots D] & \end{array}$$

in which k_c^S and k_c^T are the contact recombination constants of the different channels, while $W_I(r)$ is the rate of ionization (forward electron transfer at distance r), and $\bar{\varphi}$ is the average quantum yield of the free ions.

The difference between the products of recombination from the singlet and triplet states of the pair was also observed in some other systems. In particular, the minor T-channel contribution was determined when the recombination from the S and T states of the pair led to the formation of different isomers of the same molecule.[6,7]

The key question is, What is the mechanism of spin conversion in the RIP? In the paramagnetic complexes containing heavy atoms[8−11] the mixing of the singlet and triplet states of the RIPs in a zero magnetic field is stochastic, induced by spin relaxation (hyperfine interaction (HFI) is negligible).[12] Here we turn to the HFI mechanism, which is common for organic radical pairs. There, the hyperfine coupling constants lie in the range of 0.02−20 ns^{-1} (1−1000 G), thus they are much larger than the relaxation rates, which are inverse in $T_2 \approx T_1 \sim 1\ \mu$s. Assuming that $T_1 = T_2 = \infty$, we will consider the double-channel recombination of RIPs containing a single magnetic nucleus with spin 1/2 in the contact approximation for recombination rates and exchange interaction. The yields of the free radicals as well as the singlet and triplet products of recombination will be calculated at any initial separation and arbitrary exchange integral. All the results are expressed via the Green functions of the stochastic encounter motion of radicals. For some types of this motion, there are exact analytical expressions or approximations. The rest can be easily calculated numerically.

The outline of this paper is as follows: In the next section, the yields of the singlet and triplet products of contact recombination, φ_S and φ_T, are related to the density matrix of the RIP and expressed via the efficiencies of recombination through these channels, Z_S and Z_T. In section III, the conventional equation of motion for the density matrix is replaced by the integral equation for its Laplace transformation, with a kernel containing the Green function $\hat{G}_0$ that represents the free motion

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of the radicals of the RIP and their spin evolution without accounting for spin exchange interaction and recombination.

In the contact approximation for the reaction rates and exchange interaction, this equation is reduced in section IV to an algebraic one, and the quantum yields are expressed through its solution at the contact distance. The important new relationship between the quantum yields of the double-channel recombination is established here.

The simplest system with a single nucleus is considered in section V to calculate the Laplace transformation of operator $\hat{G}_0$ and express the recombination efficiencies Z_S and Z_T through its components. These efficiencies also obey the first established general relationship, which allows for the expression of each of them through the single total efficiency of recombination Z.

This parameter, calculated in section VI for the arbitrary initial separation of radicals, is a complex function of both reaction constants and the spin exchange parameter, j_c, calculated in the contact approximation. Considered separately are the opposite limits when this parameter is either zero or infinitely large.

In the highly polar solvents studied in section VII, the difference between these limits is not found to be considerable, at least in the spin-independent case when the recombination rates are equal. At infinitely high rates, the spin exchange does not affect the recombination yields at all. Moreover, their nontrivial diffusional dependence is very similar to that obtained earlier within the incoherent (rate) model of spin conversion provided, that the conversion rate is properly related to the HFI constant A. The sharp features in this dependence at short starting distances indicate that the theory, assuming recombination to be contact, is unsuitable for the closest starts and too slow for diffusion where the recombination is actually static.

In section VIII, the greatly simplified analytic results are obtained for the contact starts of RIPs in highly polar solvents. These general results reproduce all the particular cases studied under such assumptions earlier: single-channel recombination from either the singlet or triplet state, as well as double-channel recombination at equal rates (spin-independent total recombination). This is done in all cases for zero and infinitely large spin exchange, and the results are compared with their incoherent analogues if available. The difference is not qualitative and is rather weakly pronounced if the rate of spin conversion is properly related to the hyperfine splitting in the electron paramagnetic resonance (EPR) spectra.

II. Singlet and Triplet Products of RIP Recombination

The density matrix of the radical pair, depending on the interradical distance r and time t, obeys the following evolution equation:[13,14]

$$\frac{\partial\rho(r,t)}{\partial t} = \hat{L}\rho(r,t) + \hat{\mathscr{L}}\rho(r,t) - [\hat{W}(r) + i\hat{J}(r)]\rho(r,t) \tag{2.1}$$

with a reflective boundary condition at the contact distance $r = \sigma$, where σ equals the sum of the van der Waals radii of the radicals:

$$\hat{\jmath}\rho(r,t)|_{r=\sigma} = 0 \tag{2.2}$$

Here, $\hat{L}$ is the operator, diagonal in the Liouville space, which describes the relative stochastic motion of the radicals, while $\hat{\mathscr{L}}$ is a Liouville operator describing the distance-independent part of the spin interactions, and $\hat{\jmath}$ is a flux operator. In general, the operator $\hat{\mathscr{L}}$ includes the paramagnetic relaxation of the radical spins, the HFIs of the unpaired electron spins with nucleus spins (given by a known Hamiltonian $\hat{H}$), and the Zeeman interactions with an external magnetic field. The rate operator $\hat{W}(r)$ represents the radicals recombination, and $i\hat{J}(r)$ accounts for the exchange interaction of their spins. Both of these operators depend on the distance between the radicals, r. The recombination occurs from either the singlet or triplet state of the RIP or from them both. Thus one can specify the total recombination operator in the following way:

$$\hat{W}(r) = \hat{W}_S(r) + \hat{W}_T(r) \tag{2.3}$$

Here, $\hat{W}_S(r)$ and $\hat{W}_T(r)$ are the operators of recombination from the singlet and triplet states. Their action on the density matrix ρ is defined by the following:

$$\hat{W}_S(r)\rho = \frac{w_S(r)}{2}(\hat{P}_S\rho + \rho\hat{P}_S) \tag{2.4}$$

$$\hat{W}_T(r)\rho = \frac{w_T(r)}{2}(\hat{P}_T\rho + \rho\hat{P}_T) \tag{2.5}$$

where $w_S(r)$ and $w_T(r)$ are the recombination rates from the singlet and triplet states of the RIP, respectively, and $\hat{P}_S$ and $\hat{P}_T$ are the projection operators onto the singlet and triplet states of the RIP, respectively. They can be specified through the spin operators of the radicals of the RIP, $\vec{S}_1 = (S_{1x}, S_{1y}, S_{1z})$ and $\vec{S}_2 = (S_{1x}, S_{1y}, S_{1z})$, in the following way:

$$\hat{P}_S = \frac{\hat{E}}{4} - \vec{S}_1\vec{S}_2 \tag{2.6}$$

and

$$\hat{P}_T = \frac{3\hat{E}}{4} + \vec{S}_1\vec{S}_2 \tag{2.7}$$

in which $\hat{E}$ is the unity matrix. Obviously the quantum yield of the singlet products φ_S can be defined as follows:

$$\varphi_S = Tr\left(\int_0^\infty \mathrm{d}t \int_\sigma^\infty \hat{W}_S(r)\rho(r,t)\mathrm{d}^3r\right) = \int_0^\infty \mathrm{d}t \int_\sigma^\infty w_S(r)\rho_{SS}(r,t)\mathrm{d}^3r \tag{2.8}$$

Here, $\rho_{SS}(r,t)$ is the singlet state population of the RIP. The quantum yield of the triplet products φ_T is defined in a similar way:

$$\varphi_T = Tr\left(\int_0^\infty \mathrm{d}t \int_\sigma^\infty \hat{W}_T(r)\rho(r,t)\mathrm{d}^3r\right) = \int_0^\infty \mathrm{d}t \int_\sigma^\infty \hat{W}_T(r)(\rho_{T_0T_0}(r,t) + \rho_{T_+T_+}(r,t) + \rho_{T_-T_-}(r,t))\,\mathrm{d}^3r \tag{2.9}$$

in which $\rho_{T_0T_0}(r,t)$, $\rho_{T_+T_+}(r,t)$, and $\rho_{T_-T_-}(r,t)$ are the populations of the T_0, T_+ and T_- states, respectively.

The quantum yields of the recombination products expressed through the Laplace transform of the density matrix, $\tilde{\rho}(r,s) = \int_0^\infty \rho(r,t)\exp(-st)\mathrm{d}t$, can be presented as follows:

$$\varphi_S = Tr\left(\int_\sigma^\infty \hat{W}_S(r)\tilde{\rho}(r,0)\mathrm{d}^3r\right) = \int_\sigma^\infty w_S(r)\tilde{\rho}_{SS}(r,0)\mathrm{d}^3r, \tag{2.10}$$

for the singlet products, and

$$\varphi_T = Tr\left(\int_\sigma^\infty \hat{W}_T(r)\tilde{\rho}(r,0)d^3r\right) = \int_\sigma^\infty w_T(r)[\tilde{\rho}_{T_0T_0}(r,0) + \tilde{\rho}_{T_+T_+}(r,0) + \tilde{\rho}_{T_-T_-}(r,0)]\,\mathrm{d}^3r \tag{2.11}$$

for the products in the excited triplet state. The rest are the free radicals that escape from the cage with the yield

$$\varphi = 1 - \varphi_S - \varphi_T \qquad (2.12)$$

It is common to use their efficiencies instead of the yields, which are introduced by the following definitions:[5,15]

$$\varphi = \frac{1}{1 + Z/D},\ \varphi_T = \frac{Z_T/D}{1 + Z/D},\ \varphi_S = \frac{Z_S/D}{1 + Z/D} \qquad (2.13)$$

in which the total efficiency of the recombination is

$$Z = Z_S + Z_T \qquad (2.14)$$

The efficiency parameter Z was introduced in the spinless theory[16] instead of the recombination rate in a cage, k_{-et}, used in the old "exponential model"[12,17,18] (see ref 12, sections III(D) and V(B)). However, the separation of Z into two spin components was introduced rather recently, when the double-channel recombination was subjected to theoretical investigation.[5]

III. Distant Start

It is convenient to introduce the operator

$$\hat{U}(r) = \hat{W}(r) + i\,\hat{J}(r) \qquad (3.1)$$

which assembles together the rate and exchange operators. Then eq 2.1 can be rewritten as follows:

$$\frac{\partial\rho(r,t)}{\partial t} = \hat{L}\rho(r,t) + \hat{\mathscr{L}}\rho(r,t) - \hat{U}(r)\rho(r,t) \qquad (3.2)$$

The Laplace transformation of this equation takes the following form:

$$s\tilde{\rho}(r,s) - \rho(r,0) = \hat{L}\tilde{\rho}(r,s) + \hat{\mathscr{L}}\tilde{\rho}(r,s) - \hat{U}(r)\tilde{\rho}(r,s) \qquad (3.3)$$

in which $\rho(r,0)$ is the distribution of the density matrix over the initial separation of the radicals in a pair. If the RIPs are created at a fixed distance r_0, then the normalized initial distribution of them in the spherically symmetric case (no anisotropy of recombination and exchange interaction) is given by:

$$\rho(r,0) = \frac{\delta(r - r_0)}{4\pi r^2}\rho_0,\ \rho_0 = |S><S| \qquad (3.4)$$

Taking this into account, we can recast eq 3.3 as follows:

$$\hat{L}\tilde{\rho}(r,r_0,s) + (\hat{\mathscr{L}} - s\hat{E})\tilde{\rho}(r,r_0,s) = -\frac{\delta(r - r_0)}{4\pi r^2}\rho_0 + \hat{U}(r)\tilde{\rho}(r,r_0,s) \qquad (3.5)$$

Here, the argument r_0 in the Laplace transformation of the density matrix $\tilde{\rho}(r, r_0, s)$ is added just to stress the parametric dependence of the density matrix on the initial starting distance r_0. There are two solution methods available to solve eq 3.5. One of them employs the adjoint (or conjugated) Liouville equation (see eq 3.218 in ref 15, and refs 154 and 155 therein). This method was generalized and also extended to spin-dependent problems by Pedersen and Christensen.[19] In the present work, we use another one − the direct Green's function method.

Let us introduce the matrix Green function (without reaction and spin exchange), $\hat{G}_0(r, r', t)$, which takes into account the system motion in the coordinate and spin state but without reaction and spin exchange. It obeys the following equation with displayed initial and boundary conditions:

$$\frac{\partial\hat{G}_0}{\partial t} = \hat{L}\hat{G}_0 + \hat{\mathscr{L}}\hat{G}_0, \quad \text{at} \quad \hat{G}_0(r,r',0) = \frac{\delta(r - r')}{4\pi r^2}\hat{E},$$
$$\hat{j}\hat{G}_0(r,r',t)|_{r=\sigma} = 0 \qquad (3.6)$$

The Laplace transformation of this equation yields

$$\hat{L}\tilde{\hat{G}}_0(r,r',s) + (\hat{\mathscr{L}} - s\hat{E})\tilde{\hat{G}}_0(r,r',s) = -\frac{\delta(r - r')}{4\pi r^2} \qquad (3.7)$$

Using this Green function, eq 3.5 can be formally resolved with respect to $\tilde{\rho}(r, r_0, s)$ in the following way:

$$\tilde{\rho}(r,r_0,s) = \tilde{\hat{G}}_0(r,r_0,s)\rho_0 - \int_\sigma^\infty \tilde{\hat{G}}_0(r,r',s)\hat{U}(r')\tilde{\rho}(r'r_0,s)\mathrm{d}^3r' \qquad (3.8)$$

IV. Contact Approximation for the Recombination and Spin Exchange

Assuming that the recombination, as well as the exchange interaction, takes place only in a very narrow strip around the contact, $\sigma \le r \le \sigma + \Delta$, where the strip width $\Delta \ll \sigma$, one can estimate in the contact approximation the integral in the right-hand side of eq 3.8:

$$\int_\sigma^\infty \tilde{\hat{G}}_0(r,r',s)\hat{U}(r')\tilde{\rho}(r',r_0,s)\mathrm{d}^3r' \approx \tilde{\hat{G}}_0(r,\sigma,s)\hat{Q}\rho(\sigma,r_0,s) \qquad (4.1)$$

in which

$$\hat{Q} = 4\pi\sigma^2\Delta\cdot\hat{U}(\sigma) \qquad (4.2)$$

Because of contact simplification, the integral eq 3.8 reduces to the algebraic matrix equation for $\tilde{\rho}(\sigma, r_0, s)$:

$$\tilde{\rho}(\sigma,r_0,s) = \tilde{\hat{G}}_0(\sigma,r_0,s)\rho_0 - \tilde{\hat{G}}_0(\sigma,\sigma,s)\cdot\hat{Q}(\sigma)\tilde{\rho}(\sigma,r_0,s) \qquad (4.3)$$

Resolving eq 4.3 with respect to the density matrix, one finally obtains

$$\tilde{\rho}(\sigma,r_0,s) = [\hat{E} + \tilde{\hat{G}}_0(\sigma,\sigma,s)\cdot\hat{Q}]^{-1}\tilde{\hat{G}}_0(\sigma,r_0,s)\rho_0 \qquad (4.4)$$

This important result was obtained by Purtov and Doktorov.[20] It provides the exclusively convenient formal procedure for the calculation of the quantum yields.

In the contact approximation, the quantum yields of the singlet and triplet products of recombination are expressed through the Laplace transformation of the density matrix at contact, $\tilde{\rho}(\sigma, r_0, 0)$:

$$\varphi_S(r_0) = Tr\int_\sigma^\infty \hat{W}_S(r)\tilde{\rho}(r,r_0,0)\mathrm{d}^3r = \int_\sigma^\infty w_S(r)\tilde{\rho}_{SS}(r,r_0,0)d^3r \approx k_c^S\tilde{\rho}_{SS}(\sigma,r_0,0) \qquad (4.5)$$

and

$$\varphi_T(r_0) = Tr\int_\sigma^\infty \hat{W}_T(r)\tilde{\rho}(r,r_0,0)\mathrm{d}^3r \approx k_c^T\,[\tilde{\rho}_{T_0T_0}(\sigma,r_0,0) + \tilde{\rho}_{T_+T_+}(\sigma,r_0,0) + \tilde{\rho}_{T_-T_-}(\sigma,r_0,0)] \qquad (4.6)$$

where

$$k_c^S = 4\pi\sigma^2\Delta\cdot w_s(\sigma),\ k_c^T = 4\pi\sigma^2\Delta\cdot w_T(\sigma) \qquad (4.7)$$

The lower index c indicates that these estimates are obtained in the contact approximation of the recombination rates.

Let us show that, between these yields, the following general relationship exists, in addition to eq 2.12:

$$\frac{\varphi_S(r_0)}{k_c^S} + \frac{\varphi_T(r_0)}{k_c^T} = \tilde{\phi}(\sigma,r_0,0) - \tilde{\phi}(\sigma,\sigma,0)[1 - \varphi(r_0)] \quad (4.8)$$

in which $\tilde{\phi}(r,r_0,s)$ is the Laplace transformation of the scalar function $\phi(r,r_0,t)$ which obeys the following equation:

$$\frac{\partial\phi(r,r_0,t)}{\partial t} = \hat{L}\phi(r,r_0,t), \text{ where } \phi(r,r_0,0) = \frac{\delta(r - r_0)}{4\pi r^2} \text{ and } \hat{\jmath}\phi(r,r_0,t)|_{r=\sigma} = 0 \quad (4.9)$$

It is obvious that its Laplace transformation, $\tilde{\phi}(r, r_0, 0)$, obeys the equation

$$\hat{L}\tilde{\phi}(r,r_0,0) = -\frac{\delta(r - r_0)}{4\pi r^2} \quad (4.10)$$

As follows from eqs 4.5 and 4.6,

$$\frac{\varphi_S(r_0)}{k_c^S} + \frac{\varphi_T(r_0)}{k_c^T} = Tr\{\tilde{\rho}(\sigma,r_0,0)\} \quad (4.11)$$

To prove the relationship in eq 4.8, let us find the trace in the right-hand side of the last equation in another way. Rewriting eq 3.3 after taking eq 3.4 into account, one has, at $s = 0$,

$$\hat{L}\tilde{\rho}(r,r_0,0) = -\hat{\mathscr{L}}\tilde{\rho}(r,r_0,0) + \hat{U}(r)\tilde{\rho}(r,r_0,0) - \frac{\delta(r - r_0)}{4\pi r^2}\rho_0 \quad (4.12)$$

The general solution of this equation can be expressed through the Green function of eq 4.10, $\tilde{\phi}(r, r_0, 0)$:

$$\tilde{\rho}(r,r_0,0) = \tilde{\phi}(r,r_0,0)\rho_0 + \int \tilde{\phi}(r,r',0)\hat{\mathscr{L}}(r')\tilde{\rho}(r',r_0,0)dV' - \int \tilde{\phi}(r,r',0)\hat{W}(r')\tilde{\rho}(r',r_0,0)\mathrm{d}V' - -i \int \tilde{\phi}(r,r',0)\hat{J}(r')\tilde{\rho}(r',r_0,0)\mathrm{d}V' \quad (4.13)$$

It follows from this solution that

$$Tr\{\tilde{\rho}(r,r_0,0)\} = \phi(r,r_0,0) - \int \phi(r,r',0)Tr\{\hat{W}(r')\tilde{\rho}(r',r_0,0)\}\mathrm{d}^3r' \quad (4.14)$$

because of the following identities:

$$Tr\{\hat{\mathscr{L}}(r')\tilde{\rho}(r',r_0,0)\} = Tr\{\hat{J}(r')\tilde{\rho}(r',r_0,0)\} = 0,\ Tr(\rho_0) = 1 \quad (4.15)$$

Taking into account that $\hat{W} = \hat{W}_S + \hat{W}_T$ and setting $r = \sigma$, one obtains in the contact approximation from eq 4.14

$$Tr\{\tilde{\rho}(\sigma,r_0,0)\} = \phi(\sigma,r_0,0) - \phi(\sigma,\sigma,0)[\varphi_S(r_0) + \varphi_T(r_0)] \quad (4.16)$$

where $\varphi_S(r_0)$ and $\varphi_T(r_0)$ are given in eqs 4.5 and 4.6, and their sum is equal to $1 - \varphi(r_0)$. Combining now eqs 4.16 and 4.11, we arrive at eq 4.8.

V. Spin Dynamics in a Zero Magnetic Field

The quantum yields of the singlet and triplet products are expressed through the density matrix $\tilde{\rho}(r, r_0, s)$ at $r = \sigma$ and $s = 0$. Generally, $\tilde{\rho}(r, r_0, s)$ can be expressed, as in eq 4.4, via the Green function $\tilde{\hat{G}}_0(r, r_0, s)$, which is the Laplace transformation of

$$\hat{G}_0(r,r_0,t) = \mathrm{e}^{\hat{\mathscr{L}}t}\phi(r,r_0,\mathrm{t}) \quad (5.1)$$

Thus, the time-dependent Green function $\hat{G}_0(r, r_0, t)$ is the product of $\phi(r, r_0, t)$ defined in eq 4.9, which depends solely on the relative motion of radicals and their separation, and the matrix $e^{\hat{\mathscr{L}}t}$, which is distance independent and determined by the spin interactions only.

The Laplace transformation of eq 5.1 yields

$$\tilde{\hat{G}}_0(r,r_0,s) = \int_0^\infty \mathrm{e}^{-st}\mathrm{e}^{\hat{\mathscr{L}}t}\phi(r,r_0,t)\mathrm{d}t \quad (5.2)$$

The Liouville matrix $\hat{\mathscr{L}}$ can be reduced to a diagonal form:

$$\hat{\mathscr{L}} = \hat{T}\hat{\Lambda}\hat{T}^{-1} \quad (5.3)$$

in which $\hat{\Lambda}$ is the diagonal matrix with elements λ_1, λ_2, $\cdots$. Then obviously,

$$\tilde{\hat{G}}_0(r,r_0,s) = \hat{T}\,\tilde{\hat{\mathscr{G}}}\hat{T}^{-1} \quad (5.4)$$

where matrix $\tilde{\hat{\mathscr{G}}}$ is given by the following expression:

$$\tilde{\hat{\mathscr{G}}} = \begin{pmatrix} \tilde{\phi}(r,r_0,s - \lambda_1) & 0 & 0 \\ 0 & \tilde{\phi}(r,r_0,s - \lambda_2) & 0 \\ 0 & 0 & \cdots \end{pmatrix} \quad (5.5)$$

Thus we see that all the results can finally be expressed through the function $\tilde{\phi}(r, r_0, s)$. Moreover, for the yield calculations, very often one needs only its particular value at the contact arguments, $r = r_0 = \sigma$. At continuous diffusion in the Coulomb attraction potential, a nice analytical approximation for $\tilde{\phi}(\sigma,\sigma, s)$ obtained in ref 21 is given in Appendix A.

For the particular case of continuous diffusion in a highly polar solvent (no Coulomb attraction/repulsion in the RIP), this function is well known:[22]

$$\tilde{\phi}(\sigma,r_0,s) = \frac{1}{4\pi\sigma D}\cdot\frac{\sigma}{r_0}\cdot\frac{\exp\left(-\sqrt{\frac{s}{D}}(r_0 - \sigma)\right)}{1 + \sqrt{\frac{s\sigma^2}{D}}} \quad (5.6)$$

Here, D is the encounter diffusion coefficient, which equals the sum of the diffusion coefficients of A^- and D^+. (The Laplacian operator of the encounter diffusion in this case is $\hat{L} = \hat{E}\cdot D\Delta$.) At the start of contact, this expression reduces to the simplest one:

$$\tilde{\phi}(\sigma,\sigma,s) = \frac{1}{4\pi\sigma D}\frac{1}{1 + \sqrt{\frac{s\sigma^2}{D}}} \quad (5.7)$$

A. One-Nucleus RIP. Now let us consider the RIP containing only one nucleus with spin 1/2, located on the radical named 1. The Hamiltonian $\hat{H}$ of the HFI between the electron and nuclear spins at this radical is given by

$$\hat{H} = A\cdot\hat{\vec{I}}\cdot\hat{\vec{S}}_1 \tag{5.8}$$

in which A is the hyperfine coupling constant, and $\hat{\vec{I}}$ is the nucleus spin operator: $\hat{\vec{I}} = (\hat{I}_x, \hat{I}_y, \hat{I}_z)$. The spin basis of the RIP consists of eight wave functions. Let α and β represent the wave functions of spin directed along or opposite to the z axis, respectively. Then the direct product of three individual spin functions constitutes the single wave function of the RIP, and there are eight independent combinations of such sort:

$$\alpha_e\alpha_e\alpha_N,\ \alpha_e\alpha_e\beta_N,\ \alpha_e\beta_e\alpha_N,\ \beta_e\alpha_e\alpha_N,\ \alpha_e\beta_e\beta_N,\ \beta_e\alpha_e\beta_N,\ \beta_e\beta_e\alpha_N,\ \beta_e\beta_e\beta_N$$

Here, the subindex "e" relates to the electron spin functions, and "N" relates to the nuclear ones. The first spin function (α_e or β_e) corresponds to the electron spin of the first radical, while the following one corresponds to the second radical. The last is the spin function of the nucleus belonging to the first of the two radicals in a pair. The spin Hamiltonian $\hat{H}$ and the projection operators $\hat{P}_S$ and $\hat{P}_T$ in eq 2.4 commute with the operator of the summary z projections of the spins,

$$\hat{\Sigma}_z = \hat{S}_{1z} + \hat{S}_{2z} + \hat{I}_z$$

This allows us to subdivide the whole spin system into four ensembles that differ from each other by the z projection of the total spin:

1. $\alpha_e\alpha_e\alpha_N$, $\Sigma_z = 3/2$
2. $\alpha_e\alpha_e\beta_N$, $\alpha_e\beta_e\alpha_N$, $\beta_e\alpha_e\alpha_N$, $\Sigma_z = 1/2$
3. $\alpha_e\beta_e\beta_N$, $\beta_e\alpha_e\beta_N$, $\beta_e\beta_e\alpha_N$, $\Sigma_z = -1/2$
4. $\beta_e\beta_e\beta_N$, $\Sigma_z = -3/2$

Since we restrict our consideration to the RIP born in the singlet state, the triplet states $\alpha_e\alpha_e\alpha_e$ and $\beta_e\beta_e\beta_e$ are not populated initially and will not be because they do not mix with the other states. The ensembles 2 and 3 also do not mix with the others, but evolve independently. Thus, it turns out that, for the quantum yield calculation, one needs to specify only the evolution of ensemble 2. The results for the quantum yield obtained from ensemble 3 should be the same because ensembles 2 and 3 differ only by the sign of the total spin projection. Therefore, from this point forward, we will confine our discussion to ensemble 2.

One can also use another set of wave functions that are the orthogonal linear combinations of those included in set 2. For instance, the projection operators have a simpler form in the singlet−triplet basis of the electron spins supplemented with a nuclear one. The electron spin basis consists of one singlet and three triplet wave functions:

$$|S\rangle = \frac{1}{\sqrt{2}}(\alpha_e\beta_e - \beta_e\alpha_e), \quad |T_+\rangle = \alpha_e\alpha_e$$
$$|T_0\rangle = \frac{1}{\sqrt{2}}(\alpha_e\beta_e + \beta_e\alpha_e), \quad |T_-\rangle = \beta_e\beta_e \tag{5.9}$$

while the total spin basis of the RIP with $\Sigma_z = 1/2$ is the following:

$$S\alpha_N,\ T_0\alpha_N,\ T_+\beta_N \tag{5.10}$$

The projection operators $\hat{P}_S$ and $\hat{P}_T$ in this basis have the simplest matrix form:

$$\hat{P}_S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{P}_T = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{5.11}$$

In the same basis, the Hamiltonian eq 5.1 has the following form:

$$\hat{H} = \begin{pmatrix} 0 & A/4 & -(A/2\sqrt{2}) \\ A/4 & 0 & A/2\sqrt{2} \\ -(A/2\sqrt{2}) & A/2\sqrt{2} & -(A/4) \end{pmatrix} \tag{5.12}$$

However, to make use of eq 4.4, we have to pass to the Liouville space. The matrix elements of the Liouville operator $\hat{\mathscr{L}}$ are expressed through the Hamiltonian matrix elements as follows:

$$\hat{\mathscr{L}}_{ik,pq} = -i\hat{H}_{ip}\delta_{kq} + i\hat{H}_{qk}\delta_{ip} \tag{5.13}$$

where i, k, p, and q enumerate all the states of the basis eq 5.10, and δ_{ip} and δ_{kq} are Kroneker symbols. The dimensionality of the Liouville operator of ensemble 2 is 9 × 9.

The Hamiltonian of the contact exchange interaction is

$$J(\sigma)\hat{\vec{S}}_1\hat{\vec{S}}_2 = \hat{H}' \tag{5.14}$$

Then the corresponding part of the Liouville operator $\hat{U}$ can be represented as follows:

$$-i\hat{J}_{ik,pq} = -i\hat{H}'_{ip}\delta_{kq} + i\hat{H}'_{qk}\delta_{ip} \tag{5.15}$$

According to eq 2.4, the Liouville operator of the contact recombination from the singlet state is

$$\hat{W}_S(\sigma)_{ik,pq} = \frac{w_S(\sigma)}{2}[(\hat{P}_S)_{ip}\delta_{kq} + (\hat{P}_S)_{qk}\delta_{ip}] \tag{5.16}$$

The operator $\hat{W}_T(\sigma)$ is defined in the same way. We have to use both $\hat{W}_S(\sigma)$ and $\hat{W}_T(\sigma)$, as well as $i\hat{J}$, in eq 3.1, specifying $\hat{U}(\sigma)$ and then $\hat{Q}$ from eq 4.2, which appears in the final matrix solution (eq 4.4).

To find the operator $\tilde{\hat{G}}_0(\sigma, r_0, s)$ from eq 5.4, one needs to have the diagonal operator $\tilde{\hat{\mathscr{G}}}$ (σ, r_0, s) specified via the eigenvalues λ_i of operator $\hat{\mathscr{L}}$ defined in eq 5.3. These eigenvalues expressed through the three eigenvalues of the Hamiltonian eq 5.12 ($E_1 = -(3/4)A$, $E_2 = E_3 = (1/4)A$) are equal to their pair differences, $E_i - E_j$ ($i, j = 1, 2, 3$). Correspondingly, there are nine eigenvalues of the Liouville operator $\hat{\mathscr{L}}$:

$$\lambda_1 = \lambda_5 = \lambda_6 = \lambda_8 = \lambda_9 = 0;\ \lambda_4 = \lambda_7 = A;\ \lambda_2 = \lambda_3 = -A \tag{5.17}$$

Therefore, the elements of the operator $\tilde{\hat{\mathscr{G}}}$ and, consequently, those of operator $\tilde{\hat{G}}(r, r_0, s)$, are expressed through only three functions: $\tilde{\phi}(r, r_0, s)$, $\tilde{\phi}(r, r_0, s - iA)$, and $\tilde{\phi}(r, r_0, s + iA)$.

From this point forward, instead of these three functions, we will use the following quantities:

$$P = \mathrm{Re}\,\tilde{\phi}(\sigma,r_0,iA),\ Q = \mathrm{Im}\,\tilde{\phi}(\sigma,r_0,iA),\ F = \tilde{\phi}(\sigma,r_0,0) \quad (5.18)$$

and

$$p = \mathrm{Re}\,\tilde{\phi}(\sigma,\sigma,iA),\ q = \mathrm{Im}\,\tilde{\phi}(\sigma,\sigma,iA),\ f = \tilde{\phi}(\sigma,\sigma,0) \quad (5.19)$$

The quantum yields depend on these quantities, which is in line with the recombination and spin exchange parameters at contact.

B. Recombination Efficiencies. With these notations and the definitions given in eq 2.13, and the result of eq 4.8 can be represented now in another form:

$$\frac{\tilde{Z}_S}{k_c^S} + \frac{\tilde{Z}_T}{k_c^T} = F + \tilde{Z}(F - f) \quad (5.20)$$

in which $\tilde{Z} = Z/D$, $\tilde{Z}_S = Z_S/D$, and $\tilde{Z}_T = Z_T/D$. Accounting for eq 2.14, we obtain from here

$$\tilde{Z}_S = k_c^S \frac{k_c^T F - \tilde{Z}[1 + k_c^T(f - F)]}{k_c^T - k_c^S} \quad (5.21)$$

$$\tilde{Z}_T = k_c^T \frac{k_c^S F - \tilde{Z}[1 + k_c^S(f - F)]}{k_c^S - k_c^T} \quad (5.22)$$

These formulas express both $\tilde{Z}_S$ and $\tilde{Z}_T$ via $\tilde{Z}$ and the Green functions (F and f) in all cases except the very special one, the “spin-independent recombination”, when $k_c^S = k_c^T$. In this case, the numerators in the above formulas turn to zero, allowing the determination of the single quantity:

$$\tilde{Z} = \frac{k_c F}{1 + k_c(f - F)} \text{ at } k_c^S = k_c^T = k_c \quad (5.23)$$

VI. Recombination of Radicals Started Away from Contact

According to eq 2.12, the total yield of recombination, to the singlet and triplet products, is

$$\Phi(r_0) = \varphi_S(r_0) + \varphi_T(r_0) = 1 - \varphi(r_0) \quad (6.1)$$

in which the partial yields are defined in eqs 4.5 and 4.6. Let us represent the total yield (eq 6.1) through the recombination efficiency Z related to D:[12,15]

$$\Phi = \frac{\tilde{Z}}{1 + \tilde{Z}} \quad (6.2)$$

To calculate Φ from eq 6.1, one needs to find from eq 4.4 the matrix $\tilde{\rho}(\sigma, r_0, 0)$, the components of which determine $\varphi_S(r_0)$ and $\varphi_T(r_0)$ in eqs 4.5 and 4.6, respectively.

This has to be done by inserting $\tilde{\hat{G}}_0(\sigma,\sigma, s)$ and $\tilde{\hat{G}}_0(\sigma, r_0, s)$ into eq 4.4, deduced from eq 5 and expressed through $\tilde{\hat{\mathcal{G}}}(\sigma,\sigma, s)$ and $\tilde{\hat{\mathcal{G}}}(\sigma, r_0, s)$ from eq 5.5. In this very way we obtained Φ using the analytical calculations system Mathematica, but it appears that the form of Φ is too cumbersome. Fortunately, being substituted into eq 6.2, it leads to the much simpler expression for the relative recombination efficiency:

$$\tilde{Z} = \tilde{z}\frac{F/f}{1 + \tilde{z}(1 - F/f)} \quad (6.3)$$

Here, $\tilde{z} = z/D$ is given by the following expression:

$$\tilde{z} = k_c^S f + (k_c^S - k_c^T)\cdot\frac{\mathcal{A}}{\mathcal{B}} \quad (6.4)$$

Here, $\mathcal{A}$ and $\mathcal{B}$, given in Appendix B, are expressed via the recombination constants in eq 4.7 and the exchange parameter estimated in the contact approximation eq 4.2:

$$j_c = 4\pi\sigma^2\Delta J(s)$$

A. Reduction to the Spinless Theory. For the hyperfine coupling constant $A = 0$ (in the absence of spin conversion), it can be shown that $\mathcal{A}$ vanishes and

$$\tilde{z} = k_c^S f \quad (6.5)$$

As follows from eqs 5.18 and 5.19, in this case, $Q = q = 0$ and $P = F = \phi(\sigma, r_0, 0)$, but $p = f = \phi(\sigma,\sigma, 0)$. For the Coulomb interaction with the Onsager radius r_c, these quantities can be found from the well-known relationship

$$\phi(\sigma,r_0,0) = \frac{1}{4\pi r_c D}\exp\left(\frac{r_c}{\sigma}\right)\left[1 - \exp\left(-\frac{r_c}{r_0}\right)\right] \quad (6.6)$$

Therefore, z reduces to the simplest expression

$$\tilde{z} = \frac{k_c^S}{4\pi r_c D}(e^{r_c/\sigma} - 1) \quad (6.7)$$

Substituted in eq 6.3, in line with the relationship

$$\frac{F}{f} = \frac{1 - \exp(-r_c/r_0)}{1 - \exp(-r_c/\sigma)} \quad (6.8)$$

it gives $\tilde{Z}$ of the spinless theory first obtained in ref 16.

B. Yields of the Double-Channel Recombination. The result of eq 6.5 follows from eq 6.4 at any $A \neq 0$ if $k_c^S = k_c^T$. Being substituted into eq 6.3, it leads to eq 5.23. As was noted long ago,[3] the spin conversion in this case does not modulate the recombination, and therefore the results for $\Phi = 1 - \varphi$ do not differ from those valid for the spinless theory.

A different situation arises with partial quantum yields from eq 2.13 that can be represented as follows:

$$\varphi_T = \frac{\tilde{Z}_T}{1 + \tilde{Z}},\ \varphi_S = \frac{\tilde{Z} - \tilde{Z}_T}{1 + \tilde{Z}} \quad (6.9)$$

We need only $\tilde{Z}_T$ along with $\tilde{Z}$ to have both of them. Moreover, using eq 6.3 in eq 5.22, we obtain the universal expression for $\tilde{Z}_T$ via $\tilde{z}$:

$$\tilde{Z}_T = k_c^T\frac{k_c^S F - \tilde{z}\cdot F/f}{(k_c^S - k_c^T)[1 + \tilde{z}(1 - F/f)]} \quad (6.10)$$

in which $\tilde{z}$ is expressed in eq 6.4 via the ratio of $\mathcal{A}$ to $\mathcal{B}$. The expressions for both of them are given in Appendix B. In the limits of the weak and strong exchange interaction, these expressions are greatly simplified, as shown below.

1. Zero Exchange Interaction ($j_c = J = 0$). The efficiency of the total recombination $\tilde{Z}$ is expressed in eq 6.3 through $\tilde{z}$ defined in eq 6.4, which, in turn, depends on the ratio $\mathcal{A}$ to $\mathcal{B}$. In the case of zero exchange, these quantities given in

Appendix B take the following form:

$$\mathscr{A} = -6f(2 + (k_c^S + k_c^T)f)(\{[2 + (k_c^S + k_c^T)p]P + (k_c^S + k_c^T)qQ\}(1 + k_c^S f) - \{(1 + k_c^S p)[2 + (k_c^S + k_c^T)p] + k_c^S(k_c^S + k_c^T)q^2\}F) \quad (6.11)$$

$$\mathscr{B} = 6(k_c^S - k_c^T)\{[2 + (k_c^S + k_c^T)p]P + (k_c^S + k_c^T)qQ\}f[2 + (k_c^S + k_c^T)f] - 2\,\{[2 + (k_c^S + k_c^T)p]^2 + (k_c^S + k_c^T)^2q^2\}[8 + (3k_c^S + 5k_c^T)f]F \quad (6.12)$$

2. The Strongest Exchange ($j_c = J = \infty$). The total efficiency (eq 6.4) is now expressed via a rather simple ratio:

$$\frac{\mathscr{A}}{\mathscr{B}} = [3f^2[F(p + k_c^S p^2 + k_c^S q^2) - (pP + qQ)(1 + k_c^S f)]]/[3(k_c^S - k_c^T)(pP + qQ)f^2 - \{2(p^2 + q^2) + [p(6 + 3k_c^S p + 5k_c^T p) + (3k_c^S + 5k_c^T)q^2]\,f\}F]$$

The triplet quantum yield also becomes much simpler:

$$\varphi_T = [3k_c^T f[F(p + k_c^S p^2 + k_c^S q^2) - (pP + qQ)(1 + k_c^S\,f)]]/[2(p^2 + q^2) + f\{p[6 + 5\,(k_c^S + k_c{}^T)p] + 5\,(k_c^S + k_c^T)q^2 + [3k_c^T p + k_c^S p(3 + 8k_c^T p) + 8k_c^S k_c^T q^2]\,f\}]$$

VII. Polar Solvents

In high polarity solvents, the Coulomb interaction is absent ($r_c = 0$). Therefore, substituting eq 5.6 into the F and f from eqs 5.18 and 5.19, we have

$$F = \frac{1}{k_D}\frac{\sigma}{r_0}, \quad f = \frac{1}{k_D} \quad (7.1)$$

in which $k_D = 4\pi\sigma D$ is the diffusional rate constant. Because of this, all the results are greatly simplified.

Specifically, when either $A = 0$ or $k_c^S = k_c^T$, the quantity $\tilde{z}$ reduces to the expression

$$\tilde{z} = \frac{k_c^S}{k_D} \quad (7.2)$$

The substitution of eq 7.2 and the ratio $F/f = \sigma/r_0 = \gamma$ into eq 6.3 yields

$$\tilde{Z} = \frac{k_c^S}{k_D}\frac{\gamma}{1 + k_c^S/k_D\,(1 - \gamma)} \quad (7.3)$$

This is again the result of the spinless theory obtained in ref 16. The limiting cases of diffusion and kinetic control of the reaction are seen from the following equation:

$$Z = \begin{cases} \dfrac{\gamma}{1-\gamma}D & \text{diffusional geminate recombination,} \quad D \ll (1-\gamma)z \\ \gamma z & \text{kinetic geminate recombination,} \quad D \gg (1-\gamma)z \end{cases} \quad (7.4)$$

The spin-dependent effects will be considered below in the limiting cases of zero and strong exchange.

A. Zero Exchange Interaction ($j_c = J = 0$). In high polarity solvents, the general expressions of eqs 6.11 and 6.12 take the form

$$\mathscr{A} = -3(2 + k_s + k_t)\{2(1 + k_s)\{k_D Q(k_s + k_t)q - k_D P[2 + k_s + k_t + (4 + k_s + k_t)\theta + 4\theta^2]\} + 2\gamma[(1 + k_s)(2 + k_s + k_t) + (4 + 3k_s + k_t)\theta + 4\theta^2]\} \quad (7.5)$$

$$\mathscr{B} = -6(k_s - k_t)(2 + k_s + k_t)\{-k_D Q(k_s + k_t)\theta + k_D P[2 + k_s + k_t + (4 + k_s + k_t)\theta + 4\theta^2]\} + 2\gamma(8 + 3k_s + 5k_t)[(2 + k_s + k_t)^2 + 4(2 + k_s + k_t)\theta + 8\theta^2] \quad (7.6)$$

Here, the new notations have been used:

$$k_s = k_c^S/k_D, \; k_t = k_c^T/k_D \quad (7.7)$$

Additionally,

$$P = \frac{1}{k_D}\mathrm{Re}\left\{\frac{\sigma}{r_0}\cdot\frac{e^{-\psi(1+i)}}{1 + \theta(1 + i)}\right\},$$

$$Q = \frac{1}{k_D}\mathrm{Im}\left\{\frac{\sigma}{r_0}\cdot\frac{e^{-\psi(1+i)}}{1 + \theta\,(1 + i)}\right\}, \text{ and } \gamma = \frac{\sigma}{r_0}$$

in which the spin dependent parameters

$$\theta = \sqrt{\frac{A\sigma^2}{2D}} \text{ and } \psi = \sqrt{\frac{A(r_0 - \sigma)^2}{2D}}$$

determine the extent of spin conversion during the encounter time and the time of approaching contact from the remote start at $r_0 > \sigma$.

1. Spin-Independent Recombination ($k_s = k_t = k$). Let us turn to the very useful example, first analyzed in ref 3 and reconsidered in ref 5, using the incoherent model of spin conversion. Here, we are doing the same, but we are using the HFI model of coherent spin conversion in a zero magnetic field.

As was already noted, in the case of equal recombination constants, the total recombination yield and its efficiency $\tilde{Z}$ given by eq 6.3 are independent of the spin conversion. Unlike the total yield, the individual yields of triplet and singlet products are affected by spin conversion. In particular, the triplet quantum yield is

$$\varphi_T = \frac{3}{8}\gamma k\left[\frac{1}{1 + \mathrm{k}} + e^{-\psi}\cdot\frac{\theta \sin\psi - (1 + k + \theta)\cos\psi}{1 + k^2 + 2k(1 + \theta) + 2\theta(1 + \theta)}\right]$$

$$\text{in which } k = \frac{k_c}{k_D} \quad (7.8)$$

As was expected in the absence of spin conversion ($A = 0$), this yield is zero:

$$\varphi_T = 0, \text{ since } \theta = \psi = 0$$

Otherwise, $\varphi_T \neq 0$ is spin-dependent, as well as $\varphi_S = \varphi - \varphi_T$. In the important particular case of diffusion-controlled recombination, one obtains

$$\varphi_T = \frac{3}{8}\gamma(1 - e^{-\psi}\cos\psi), \text{ at } k = \infty$$

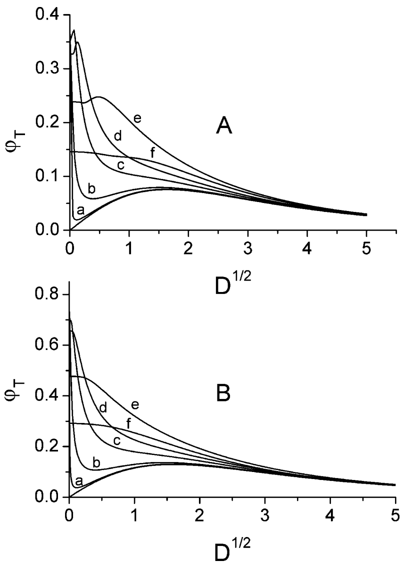

Figure 1. The triplet quantum yield as a function of diffusion at the contact start (the lowest curve) and larger starting distances; r_0 in Å: (a) 7.01, (b) 7.1, (c) 7.5, (d) 8.0, (e) 11.0, and (f) 18.00. The common parameters for coherent (A) and incoherent (B) spin conversion are the same: $k = 800$ Å^3 ns^{-1}, $\sigma = 7$ Å. At the same time, the HFI constant $A = 0.176$ ns^{-1}, while the rate of incoherent conversion $K_s = A/8 = 0.022$ ns^{-1}. D is measured in Å^2/ns.

Obviously, this function passes through the first maximum at

$$\psi = \sqrt{\frac{A(r_0 - \sigma)^2}{2D}} = \frac{3\pi}{4} \qquad (7.9)$$

There is a very transparent way to obtain eq 7.9 in the case of diffusion control, when the radical pair recombines at the very first contact. The number of RIPs recombining from their triplet state is proportional to the product of the triplet state population ρ_{TT} at instant t and the probability $\Omega(t)$ to simultaneously find the radical pair at the contact. The total population of the triplet state $\rho_{TT} = \rho_{T_+T_+} + \rho_{T_0T_0} + \rho_{T_-T_-}$, and the triplet product yield is

$$\varphi_T = \int_0^\infty \rho_{TT}(t)\Omega(t)\mathrm{d}t \qquad (7.10)$$

The density probability function of the first contact is well known:

$$\Omega(t) = \frac{\sigma(r_0 - \sigma)}{2r_0\sqrt{\pi D}} t^{-3/2} \exp\left(-\frac{(r_0 - \sigma)2}{4Dt}\right) \qquad (7.11)$$

whereas the triplet population evolving because of the Liouvillian $\mathcal{L}$ is[17,23]

$$\rho_{TT}(t) = \frac{3}{8}(1 - \cos At) \qquad (7.12)$$

Equation 7.9 follows once again from the last three expressions.

2. Coherent versus Incoherent Spin Conversion. The diffusional dependencies of the triplet quantum yield at different starting points are compared in Figure 1 with their incoherent analogues calculated according to ref 5 and presented there in Figure 7. Qualitatively, they are very similar, provided that the incoherent parameter from ref 5 $\alpha = \sqrt{4K_s\sigma^2/D} = \theta$, that is

$$K_s = A/8 \qquad (7.13)$$

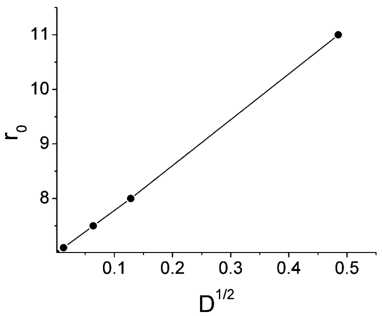

Figure 2. The linear relationship (eq 7.15) between the starting distances r_0 and positions of the maxima, on the scale $\sqrt{D}$ that the curves of $\varphi_T(\sqrt{D})$ in Figure 1A pass through.

in which K_s is the rate of incoherent transitions. However, there is a peculiarity appearing in the coherent case at the top of all the curves: the maximum shifting to the right with increasing r_0. Under diffusional control, this is the maximum seen in eq 7.9. This is the only peculiarity that manifests about the dynamic (coherent) mechanism of the spin conversion, which is periodic in time. The maximum of the triplet yield is reached, provided that the radicals born at r_0 come into contact at time π/A, when the triplet RIPs population is maximal. This condition, represented by eq 7.10, leads to the linear relationship

$$r_0 = \sigma + \frac{3\pi}{4}\sqrt{\frac{2}{A}}\cdot\sqrt{D} \qquad (7.14)$$

From this equality, one can get the value of D where the maximum is located for given r_0. Figure 2 precisely confirms this expectation: the slope calculated from eq 7.14 at $A = 0.176$ ns^{-1} is 7.87, whereas the slope obtained from the figure is equal to 8.26.

3. The Price for Contact Recombination. Having the general formula of eq 7.8 for φ_T in line with the total recombination efficiency $\tilde{Z}$ from eq 7.3, we can easily find two other efficiencies:

$$\tilde{Z}_T = \varphi_T(1 + \tilde{Z}), \tilde{Z}_S = \tilde{Z} - \tilde{Z}_T \qquad (7.15)$$

The diffusional dependence of all of them is depicted in Figure 3. Unlike the $\tilde{Z}_T$ curves, which are smooth and weakly dependent on the starting distance, the ascending (diffusional) branches of $\tilde{Z}$ in Figure 3B are affected much more by an increase in r_0. However, $\tilde{Z}_S$ is the most sensitive to very small variations in the starting distance. Its diffusional dependence is qualitatively different for the contact start and for the start insignificantly larger than it. This physically unreasonable difference is the main weakness of the contact approximation for recombination. This approximation ignores the exponential space dependence of the normal recombination rate, which cannot be narrower than the tunneling distance $L \approx 1 \pm 2$ Å. Moreover, the contact approximation ignores the static electron transfer (which remains even at $D = 0$) and therefore is not applicable to the region of small D (see Chapter V-D in ref 12). Therefore, the reliable fitting of the experimental data obtained in ref 5 should be done numerically, using the real space dependence of the electron transfer rates.

B. Infinite Exchange Interaction ($j_c = J = \infty$). In the case of the largest exchange integral, all the results are greatly simplified, and we get

$$\frac{\mathcal{A}}{\mathcal{B}} = 3\frac{(1 + k_s + \theta)\gamma - k_D(1 + k_s)(P + P\theta - Q\theta)}{3k_D(k_s - k_t)(P + P\theta - Q\theta) - (8 + 3k_s + 5k_t + 6\theta)\gamma}$$

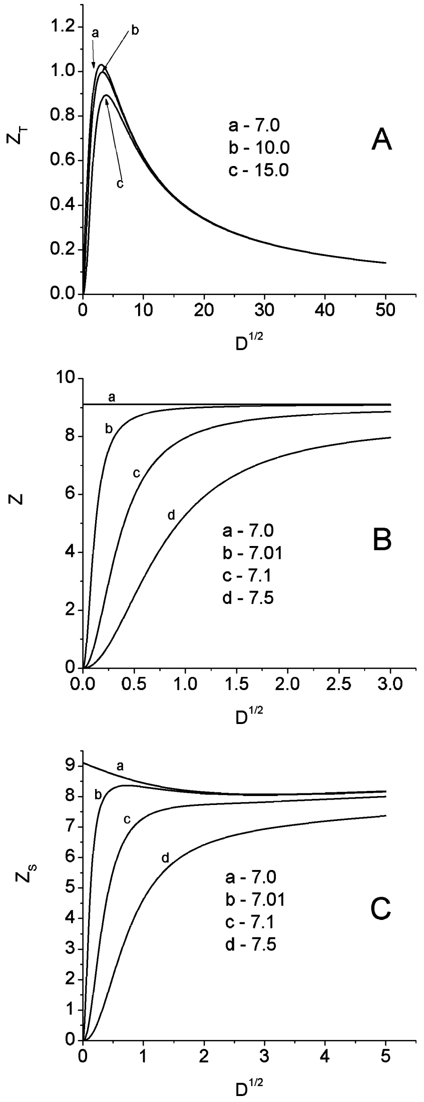

Figure 3. The diffusional dependencies of the recombination efficiencies from different starting distances r_0: (A) through the triplet channel, (B) total, and (C) through the singlet channel, at $k_c^S = k_c^T = 800$ Å^3/ns.

Using this result and the relationships of eq 7.1 in eq 6.4, one gets $\tilde{z}$ as well as $\tilde{Z}$ and $\tilde{Z}_T$ from eq 6.3 and 6.10, respectively. Having $\tilde{Z}$ and $\tilde{Z}_T$, it is easy to find any other quantum yields as well. For instance,

$$\varphi_T = 3k_t \frac{(1 + k_s + \theta)\gamma - k_D(1 + k_s)(P + P\theta - Q\theta)}{8(1 + k_s)(1 + k_t) + 3(2 + k_s + k_t)\theta}$$

This result is the same as that which follows from the earlier work of Salikhov.[24] Moreover, it was generalized there for arbitrary nuclear spin *I* and any statistics of recontacts. However, such statistics are known for only the diffusional encounter of neutral radicals, whereas, in our theory, we are using the Green functions, which can be easily calculated, for charged radicals as well, either analytically or numerically.

1. Spin-Independent Recombination. Especially simple are the results in the special case $k_s = k_t = k$, when

$$\tilde{Z} = k\frac{\gamma}{1 + k(1 - \gamma)}\ \tilde{Z}_T = 3\gamma k\frac{[(1 + k + \theta) - e^{-\psi}(1 + k)\cos\psi)}{2[1 + k(1 - \gamma)](4 + 4k + 3\theta)}$$

These efficiencies determine the quantum yields of eq 2.13:

$$\varphi = \frac{1}{1 + \tilde{Z}},\ \varphi_T = \frac{\tilde{Z}_T}{1 + \tilde{Z}},\ \varphi_S = \varphi - \varphi_T$$

The expression in eq 7.9 for φ_T is reproduced under diffusional control of the geminate recombination when

$$\tilde{Z} = \frac{\gamma}{1 - \gamma} \text{ and } \tilde{Z}_T = \frac{3}{8}\gamma\frac{1 - e^{-\psi}\cos\psi}{1 - \gamma} \text{ as } k \rightarrow \infty$$

The last results are valid at any exchange integral *J*, provided j_c is negligible compared to $k_c^S = k_c^T$.

VIII. Contact Start in Polar Solvents

The general expressions for $\varphi(r_0)$ and $\varphi_T(r_0)$ have to be averaged over the initial distribution of starting distances $f(r_0)$ created by the preceding bimolecular ionization.[15] Instead, it is often presumed that the reactants start from the contact ($r_0 = \sigma$), that is, $f(r_0) = \delta(r_0 - \sigma)/4\pi r_0^2$. This particular case is easier to study as an example because the initial stage when the reactants approach each other is eliminated.

However, this is not only a model, but also a real physical situation when the radicals are born because of short-range proton or atom transfer or bond cleavage. The same is true for chemiluminescence resulting from the backward electron transfer considered in a few recent works.[25−30] The spin conversion in the contact-born radical pair, constituted from the adamantanone anion radical $\dot{A}^-$ and methyl-*m*-oxybenzoate radical $\dot{M}$, proceeds between sequential recontacts. The initial singlet state of this RIP changes to a triplet and thus opens the way for electron transfer to a triplet product. This becomes possible parallel to the allowed RIP recombination through a singlet channel, to both the excited singlet and ground states. In this particular example, the Coulomb interaction is absent in principle ($r_c \equiv 0$), while, for the oppositely charged ion-radicals, this is the case only in highly polar solvents. Here, we address either of these cases, while the general formulas that are valid for arbitrary polarity (when $r_c \neq 0$) are presented in Appendix C.

If the radicals start from contact, then

$$F = f = 1/k_D,\ \gamma = 1, \text{ since } r_0 = \sigma \tag{8.1}$$

Hence, according to eqs 6.3 and 6.10

$$\tilde{Z} = \tilde{z} \tag{8.2a}$$

$$\tilde{Z}_T = \frac{k_t(k_s - z)}{k_s - k_t} \tag{8.2b}$$

in which

$$\tilde{z} = k_s + (k_s - k_t)\frac{k_D\mathscr{A}}{\mathscr{B}} \tag{8.3}$$

The quantities $\mathscr{A}$ and $\mathscr{B}$ are expressed through *p* and *q* in eq 5.18, the values of which with regard to eq 5.6 are in turn equal to

$$p = \frac{1}{k_D}\text{Re}\left[\frac{1}{1 + \theta(1 + i)}\right] = \frac{1}{k_D}\frac{1 + \theta}{(1 + \theta)^2 + \theta^2} \tag{8.4a}$$

$$q = \frac{1}{k_D}\text{Im}\left[\frac{1}{1 + \theta(1 + i)}\right] = -\frac{1}{k_D}\frac{\theta}{(1 + \theta)^2 + \theta^2} \tag{8.4b}$$

Finally, we have two quantities that have to be used in eq 8.3:

$$k_D\mathscr{A} = -3\theta[j^2 + (2 + k_s + k_t)(2 + k_s + k_t + 4\theta)]$$

$$\mathscr{B} = 8(1 + k_t)[j^2 + (2 + k_s + k_t)^2] + 2[3j^2 + 8j(1 + k_t) + (2 + k_s + k_t)(16 + 3k_s + 13k_t)]\theta + 8(8 + 3k_s + 5k_t)\theta^2$$

in which $j = j_c/k_D$. The results are given below for three cases, $k_s = 0$, $k_s = k_t$, and $k_t = 0$ (from top to bottom):

$$\tilde{z} = [3k_t\theta[j^2 + (2 + k_t)(2 + k_t + 4\theta)]]/ [8(1 + k_t)[j^2 + (2 + k_t)^2] + 2[3j^2 + 8j(1 + k_t) + (2 + k_t)(16 + 13k_t)]\theta + 8(8 + 5k_t)\theta^2]$$

$$\tilde{z} = k \text{ at } k_s = k_t = k$$

$$\tilde{z} = k_s - [3k_s\theta[j^2 + (2 + k_s)(2 + k_s + 4\theta)]]/ [8[j^2 + (2 + k_s)^2] + 2[j(8 + 3j) + (2 + k_s)(16 + 3k_s)]\theta + 8(8 + 3k_s)\theta^2]$$

In the absence of spin conversion ($\theta = 0$), we have either $\tilde{z} = 0$, if the recombination proceeds only through the triplet channel, or $\tilde{z} = k_s$, if only the singlet recombination channel is working. In the special intermediate case, when $k_s = k_t = k$, the recombination efficiency $\tilde{z} = k$ at any spin conversion parameter θ.

A. Zero-Spin Exchange ($j = J = 0$). In some previous works, the spin exchange was ignored, and relatively simple results were obtained for such an approximation.[5,15] Making use of it here, we also get rather simple expressions for the recombination efficiencies found in eq 8.2:

$$\tilde{Z} = k_s + [3(k_t - k_s)(2 + k_s + k_t)\theta(2 + k_s + k_t + 4\theta)]/ [8(1 + k_t)(2 + k_s + k_t)^2 + 2(2 + k_s + k_t)(16 + 3k_s + 13k_t)\theta + 8(8 + 3k_s + 5k_t)\theta^2]$$

$$\tilde{Z}_T = [3k_t(2 + k_s + k_t)\theta(2 + k_s + k_t + 4\theta)]/ [8(1 + k_t)(2 + k_s + k_t)^2 + 2(2 + k_s + k_t)(16 + 3k_s + 13k_t)\theta + 8(8 + 3k_s + 5k_t)\theta^2]$$

in which k_t and k_s are defined in eq 7.7.

Similar results for the rate (incoherent) theory of spin conversion, represented in eq 3.2 of ref 5, are even more simple. In particular, $\tilde{Z}_T$ in the incoherent theory depends only on $k_t \equiv 1/y^T$:

$$\tilde{Z}_T = \frac{3}{4}\frac{\alpha k_t}{1 + \alpha + k_t} \rightarrow \frac{3}{4}k_t \text{ at } \alpha \rightarrow \infty \tag{8.5}$$

This result is compared with its exact (coherent) analogue in Figure 4. In the absence of spin conversion ($\alpha = \theta = 0$), the triplet efficiency turns to zero in both the coherent and incoherent theories. In the opposite limit of full mixing ($\alpha = \theta = \infty$), $\tilde{Z}_T$ reaches its maximal value, which is in the present (coherent) theory:

$$\text{Max } \tilde{Z}_T = \frac{3}{8}k_t\frac{2 + k_s + k_t}{2 + \frac{3}{4}k_s + \frac{5}{4}k_t} \rightarrow \frac{3}{8}k_t \text{ at } k_s = k_t$$

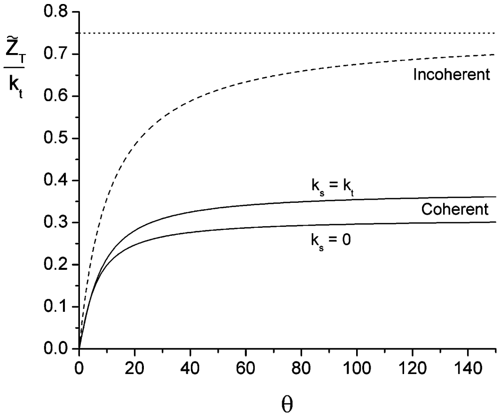

Figure 4. The spin-conversion dependence of the efficiency of recombination through the triplet channel in the rate (incoherent) theory of conversion and in the present (coherent) theory (dependent on the relationship between the recombination constants). Diffusional recombination of triplet pairs born at contact ($k_t = 10$).

but, in the spin-independent case, the result is half as much as that obtained in eq 8.5 with the model (incoherent) theory.

Under diffusion control ($k_t \gg 1$), the efficiency of recombination from only the triplet channel ($k_s = 0$) does not differ too much from that of the spin-independent case ($k_s = k_t$), but under kinetic control ($k_t \ll 1$), the difference is even less.

1. Single-Channel Recombination. If one of the recombination channels is switched off, then all the recombination is occurring through the other one. When $k_s = 0$, then we obtain

$$\tilde{Z}_T = [3k_t(2 + k_t)\theta(2 + k_t + 4\theta)]/[8(1 + k_t)(2 + k_t)^2 + 2(2 + k_t)(16 + 3 + 13k_t)\theta + 8(8 + 5k_t)\theta^2] = \tilde{Z};\ \tilde{Z}_S = 0$$

instead of the rather primitive model formula in eq 3.4 from ref 5. On the other hand, when $k_t = 0$, the recombination efficiency is

$$\tilde{Z}_S = k_s - \frac{3k_s(2 + k_s)\theta(2 + k_s + 4\theta)}{8(2 + k_s)^2 + 2(2 + k_s)(16 + 3k_s)\theta + 8(8 + 3k_s)\theta^2} = \tilde{Z};\ \tilde{Z}_T = 0$$

instead of that obtained in eq 3.3 for the model theory.[5]

The efficiency of recombination through the triplet channel monotonically increases with the spin-conversion rate A, while that for the singlet channel goes down. When one goes from $A = \theta = 0$ to $A = \theta = \infty$ (at given D) the recombination efficiencies change in the following limits:

$$0 \le \tilde{Z}_T < \frac{3}{2}k_t\frac{2 + k_t}{8 + 5k_t} \quad k_s \ge \tilde{Z}_S > k_s - \frac{3}{2}k_s\frac{2 + k_s}{8 + 3k_s} \tag{8.6}$$

In Figure 5, the variation of the recombination efficiencies between the slow and fast conversion limits is shown, taking $k_t = k_s = k \ll 1$ (kinetic recombination of the contact-born RIP). In the limit of the instantaneous spin conversion ($A \rightarrow \infty$) we obtain from eq 8.6:

$$\text{Max } Z_T = \frac{3}{8}\cdot\frac{k_c^T}{4\pi\sigma} \quad \text{Min } Z_S = \frac{5}{8}\cdot\frac{k_c^S}{4\pi\sigma}, \quad \text{at} \quad k_c^T, k_c^S \ll k_D$$

Because of the dispersion of the times between recontacts, the average cos At is zero at large A. At such a fast conversion, the

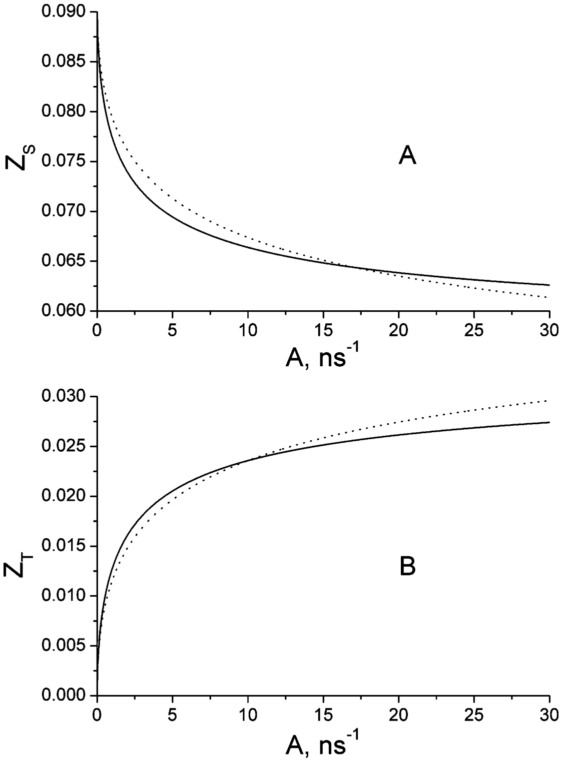

Figure 5. The retardation of singlet RIP recombination through the singlet channel (A) and the acceleration of that through the triplet one (B) with accelerating the spin conversion. Solid lines are for $J = 0$, while the dashed lines are for $J = \infty$. Other parameters: $k_c = 800$ Å^3/ns, $D = 10^{-5}$cm^2/s.

weight of the populated triplet states according to eq 7.12 is $\langle \rho_{TT} \rangle = 3/8$. Therefore, the maximal rate constant of recombination through the triplet channel is weighted in the last formula with 3/8, while the recombination through the singlet channel has the weight $1 - 3/8 = 5/8$.

Different results follow from the formulas in eq 8.6 in the opposite limit of the diffusional recombination accomplished at the first recontact:

$$\text{Max } Z_T = \frac{3}{10}\cdot\frac{k_c^T}{4\pi\sigma} \quad \text{Min } Z_S = \frac{1}{2}\cdot\frac{k_c^S}{4\pi\sigma} \quad \text{at} \quad k_c^T, k_c^S \gg k_D$$

Since they remain finite as $D \to 0$, all $\tilde{Z} = Z/D \to \infty$ and φ_T, $\varphi_S \to 1$ in the slow diffusion limit, as well as in the spinless theory.

2. Spin-Independent Recombination ($k_s = k_t = k$). At equal recombination constants, we obtain for all the quantum yields

$$\tilde{Z} = k\frac{\gamma}{1 + k(1 - \gamma)}$$

$$\tilde{Z}_T = 3\gamma k \cdot \frac{[(1 + k + \theta) - e^{-\psi}(1 + k)\cos\psi]}{2[1 + k(1 - \gamma)](4 + 4k + 3\theta)}$$

Their dependence on the HFI constant, A, as well as on the diffusion coefficient, is confined in the dimensionless parameter $\theta = \sqrt{A\sigma^2/2D}$. At given $A = 0.176$ ns^{-1} (10 G) the diffusional dependence of all the yields is presented in Figure 6. It is very similar to that obtained with the incoherent model of spin conversion in Figure 5 of ref 5. The same dependencies may be represented in another way, proposed in ref 3. The total yield of free radicals φ, used as an argument, changes from 0 to 1 with increasing diffusion. Simultaneously, the total recombination yield $\Phi = 1 - \varphi$ is represented by the diagonal of the square displayed in Figure 7. Then the single curve $\varphi_T(\varphi)$ shows not only the triplet yield, but also the singlet yield $\varphi_S = \Phi - \varphi_T$. The four $\varphi_T(\varphi)$ curves shown in Figure 7 demonstrate how the triplet yield grows when A increases with the sacrifice of singlet products.

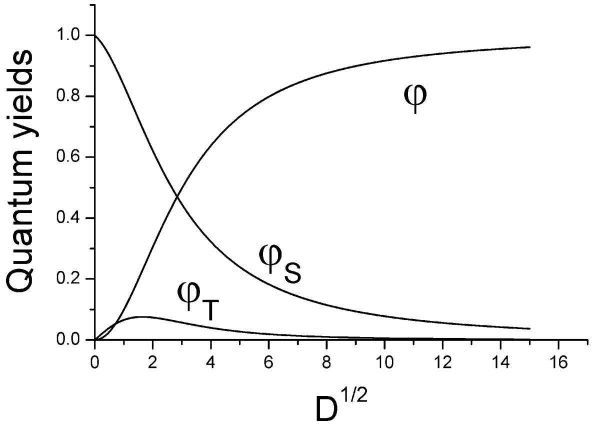

Figure 6. The diffusional variation of all the quantum yields at $A =$ 10 G with the same k_c as that shown in the previous figures.

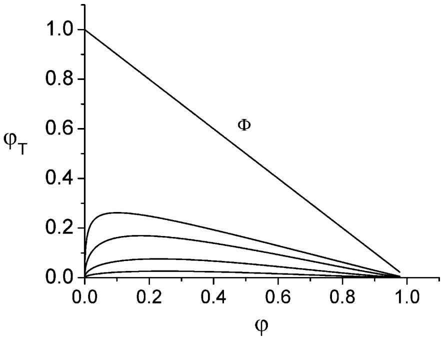

Figure 7. The dependence of the triplet quantum yield, φ_T, on the free radicals yield $\varphi = 1 - \Phi$ at different rates of spin conversion A: 1, 10, 100, and 1000 G (from bottom to top) at $k_c = 800$ Å^3/ns.

B. Infinite Exchange Interaction ($j_c = J = \infty$). This is the easiest case for study, and the corresponding results are the simplest ones:

$$\tilde{Z} = k_s + \frac{3(k_t - k_s)\theta}{8 + 8k_t + 6\theta} \quad \tilde{Z}_T = \frac{k_t}{2}\frac{\frac{3}{4}\theta}{1 + k_t + \frac{3}{4}\theta} \qquad (8.7)$$

It is interesting that $\tilde{Z}_T$ is independent of k_s, as in the model theory.[5] Moreover, the model result is functionally the same:

$$\frac{3}{4}k_t\frac{\alpha}{1 + k_t + \alpha}$$

provided α is identified with (3/4)θ. To ensure such an equality, one should take

$$\frac{A}{8} = \frac{16}{9}K_s$$

This is almost the same condition that is given in eq 7.13. Because of this choice, the $\tilde{Z}_T$ from eq 8.7 relates to its model analogue as (1/2):(3/4).

1. Single-Channel Recombination. In the case of recombination only through a triplet channel ($k_s = 0$), we have, as usual, $\tilde{Z} = \tilde{Z}_T$ defined in eq 8.7. Recombination through the solely singlet channel provides

$$\tilde{Z}_S = k_s \frac{8 + 3\theta}{8 + 6\theta} = \tilde{Z} \text{ at } k_t = 0 \tag{8.8}$$

These efficiencies, $\tilde{Z}_T$ and $\tilde{Z}_S$, are displayed by dashed lines in Figure 5, in line with those related to $J = 0$. The difference is rather insignificant at any spin-conversion rate.

Using eq 8.8, one can easily estimate the yield of pairs recombined through the singlet channel:

$$\varphi_s = 1 - \varphi = \frac{\tilde{Z}}{1 + \tilde{Z}} = \frac{k_s(8 + 3\theta)}{8(1 + k_s) + 3(2 + k_s)\theta} \tag{8.9}$$

This result coincides with that obtained by Purtov and Salikhov.[24,31]

2. Spin-Independent Recombination ($k_s = k_t = k$). When the spin exchange is infinitely fast ($J = \infty$), we obtain instead of eqs 8.7 the much simpler results

$$\varphi = \frac{1}{1 + k}, \ \varphi_T = \frac{3k\theta}{2(1 + k)(4 + 4k + 3\theta)}, \quad \varphi_S = 1 - \varphi - \varphi_T \tag{8.10}$$

Since φ is the same for any J, the whole difference between the limits $J = 0$ and $J = \infty$ reduces to the difference in the expressions for φ_T. Taking their ratio, we get the objective measure of this difference:

$$R = \frac{\varphi_T\,(J = 0)}{\varphi_T\,(J = \infty)} = \frac{(1 + k + 2\theta)(4 + 4k + 3\theta)}{4[(1 + k)(1 + k + 2\theta) + 2\theta^2]} \tag{8.11}$$

It can be seen that R changes in the very rigid limits $1 \geq R \geq 0.75$ when the hyperfine coupling constant A (and consequently θ) varies from 0 to ∞. This is the scale of the effect of the exchange interaction on the quantum yield.

IX. Conclusions

We have developed a general theory for the double-channel geminate recombination at any rate of HFI-induced spin conversion and arbitrary spin exchange between the radicals in a pair. The contact approximation for the spin exchange and recombination through both the triplet and singlet channels is the only limitation of the theory.

It should be emphasized that the partial yields of singlet and triplet products of recombination are studied in line with the yield of free radicals, to which most of the previous investigations are confined. We established the important general relationship between these yields (eq 4.8) and the analogous relationship between the partial recombination efficiencies (eq 5.20), which allows for the expression of both of them via the total one and the Green functions of the free motion.

Qualitatively, our main results are very similar to those obtained with the rate model of spin conversion in ref 5, provided there is a definite relationship between the phenomenological rate and the HFI constant established in eq 7.13. Besides this, we estimated the effect of spin exchange and found that, in polar solvents, the maximal difference in the quantum yields between the limits of zero and infinitely fast exchange is not more than 25%. The yield dependencies on diffusion, recombination rates, and the HFI constant are specified.

Although our results are valid for a pair with a single nucleus, it is pointed out in ref 24 how the effective hyperfine coupling constant should be defined to extend the theory to the many-nuclei radical pair.

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Appendix A: Green Function for Coulomb Attraction Potential

In our notations the expression for $\varphi(\sigma,\sigma,s)$ obtained in ref 21 and refined from misprints in paper[32] takes the form

$$\varphi(\sigma,\sigma,s) = \frac{1}{4\pi D\sigma} \cdot \frac{1}{\mu_0(\sigma) + \kappa(\sigma,s)} \tag{A.1}$$

where

$$\mu_0(\sigma) = \frac{1/x}{\exp(1/x) - 1}; \ \kappa(\sigma, s) = \frac{s\tau_d + [\vartheta(\sigma)/\varsigma(\sigma)]\sqrt{s\tau_d}}{\sqrt{s\tau_d} + \vartheta(\sigma)}$$

Here,

$$\varsigma(\sigma) = x^2 \exp(1/x)[1 - \exp(-1/x)]^2$$

and

$$\vartheta(\sigma) = [x^3[\exp(1/x) + \exp(-1/x) - 2] - x]/ \left[\frac{1}{6}[Ei(1/x) - \exp(1/x)(x + x^2 + 2x^3)] + \frac{1}{6}[E_1(1/x) - \exp(-1/x)(x - x^2 + 2x^3)] + \frac{2}{3}x^2 + x\right]$$

where $x = \sigma/r_c$, $\tau_d = \sigma^2/D$, and r_c is the Onsager radius, while Ei and E_1 are the integral exponential functions.

Appendix B: General Results

Generally, $\tilde{z}$ is expressed in eq 6.4 via the quantities given below:

$$\mathscr{A} = 3f\{P[4 + 2\,(k_c^S + k_c^T)p - j_c q] + [j_c\, p + 2(k_c^S + k_c^T)q]Q + k_c^S(\{2\,(k_c^S + k_c^T) + [j_c{}^2 + (k_c^S + k_c^T)^2]p\}P + \{-j_c + [j_c{}^2 + (k_c^S + k_c^T)^2]q\}Q)f^2 - \{2(1 + k_c^S p)[2 + (k_c^S + k_c^T)p] - j_c q + 2k_c^S(k_c^S + k_c^T)q^2\}F + f[P[2k_c^T + 3k_c^{S2}p + (j_c{}^2 + k_c^{T2})p + k_c^S(6 + 4k_c^T p - j_c q)] + [j_c(-1 + k_c^S p) + j_c{}^2 q + (k_c^S + k_c^T)(3k_c^S + k_c^T)q]Q - ((1 + k_c^S p)\{2(k_c^S + k_c^T) + [j_c{}^2 + (k_c^S + k_c^T)^2]p\} - j_c k_c^S q + k_c^S[j_c{}^2 + (k_c^S + k_c^T)^2]q^2)F]\}$$

$$\mathscr{B} = 3(k_c^T - k_c^S)(\{2(k_c^S + k_c^T) + [j_c{}^2 + (k_c^S + k_c^T)^2]p\}P + \{-j_c + [j_c{}^2 + (k_c^S + k_c^T)^2]q\}Q)f^2 + 2(16 + p\{16(k_c^S + k_c^T) + [j_c{}^2 + 4(k_c^S + k_c^T)^2]p\} - 8j_c q + [j_c{}^2 + 4(k_c^S + k_c^T)^2]q^2)F + f[-3(k_c^S - k_c^T)\{P[4 + 2(k_c^S + k_c^T)p - j_c q] + [j_c p + 2(k_c^S + k_c^T)q]Q\} + (6j_c{}^2 p + 3k_c^{S3}(p^2 + q^2) + k_c^{S2}[p(12 + 11k_c^T p) + 11k_c^T q^2] + k_c^T\{20 + 5p[4k_c^T + (j_c{}^2 + k_c^{T2})p] - 13\, j_c q + 5(j_c{}^2 + k_c^{T2})q^2\} + k_c^S\{12 + 32k_c^T p + 13k_c^{T2}(p^2 + q^2) + 3j_c[-q + j_c(p^2 + q^2)]\})F]$$

Appendix C: Contact Start of the RIP

1. $J = 0$

$$A = -3[2 + (k_c^S + k_c^T)f](-\{p[2 + (k_c^S + k_c^T)p]\} - (k_c^S + k_c^T)q^2 + [2 + (k_c^S + k_c^T)p]f)$$

$$B = 2(16 + p[10k_c^S + 22k_c^T + (k_c^S + k_c^T)(k_c^S + 7k_c^T)p] + (k_c^S + k_c^T)(k_c^S + 7k_c^T)q^2 + \{k_c^{S2}[p(3 + 4k_c^T p) + 4k_c^T q^2] + 2k_c^S[3 + 8k_c^T p + 4k_c^{T2}(p^2 + q^2)] + k_c^T[10 + 13k_c^T p + 4k_c^{T2}(p^2 + q^2)]\}f)$$

2. $J = \infty$

$$\frac{\mathscr{A}}{\mathscr{B}} = \frac{3f(p^2 + q^2 - pf)}{2\{p^2 + q^2 + [p(3 + 4k_c^T p) + 4k_c^T q^2]f\}}$$

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