

Electron Conduction Along Aliphatic Chains

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1. Introduction

The efficiency of photoinduced charge separation in the photosynthetic reaction center is achieved by a choice of suitable electron-transfer rates which are fast enough in the forward and slow enough in the backward direction. The separated charges seem to be paying a minimum price in terms of irreversible energy losses. The cardinal question is why the reaction center functions so efficiently. An answer to this question is tantamount to explaining which properties of the reaction center protein material are responsible for the realization of its transfer rates.

The rate of electron transfer by organic molecules in the simplest description, which assumes a separation of the motion of electron and nuclear degrees of freedom (Born-Oppenheimer approximation), is given by expressions of the type

$$\text{rate of electron-transfer} = V^2(r) f(T) \quad (1)$$

Here $f(T)$ is the Frank-Condon weighted density and describes the temperature-dependent matching of the vibrational modes of freedom of the electron acceptors and donors and their surrounding. This factor has received most attention in theoretical studies. Its classical description dates back to the 1956 work of MARCUS [1], the quantum mechanical description is due to the work of Pekar and others covered in a 1959 review [2]. A most recent review is Ref. 3.

The first factor in (1) describes the tunneling of the electron between donor and acceptor without accounting for a possible participation of vibrational degrees of freedom along its path. It originates from an overlap of the frontier electron

orbitals between donor and acceptor, where the overlap can involve intermediate virtual orbitals either of the solvent (protein) or of intramolecular groups (e.g. the chains of the reaction center chromophores). In this study we want to investigate this first factor of the electron-transfer rate, which despite its wide neglect [4] in the literature is of obvious importance, too.

Reasons for the neglect of the electron-transfer matrix element $V^2(r)$ are at least two: (1) the calculation of this element from first principles is very difficult because its magnitude is actually small compared to the natural energies of electronic states in molecules. (2) The factor cannot be altered easily by the experimentalist, the opposite being true for the Franck-Condon weighted density which varies with the temperature. Because of the poor state of knowledge on $V^2(r)$ one should not expound new theories on this term but rather contribute to its measurement. An interesting attempt has been made in this respect by POTASEK and HOPFIELD [5] who obtained information on the size of $V^2(r)$ through measurements on charge-transfer absorption.

Our approach to the electron-transfer element is through the exchange interaction $J(r)$ between paramagnetic groups. The exchange interaction of two doublet molecules measures the energy separation of the singlet and the triplet states in which such pairs can exist. This exchange energy is related to the electron transfer matrix element by the expression

$$J(r) = V^2(r) g \quad (2)$$

where the factor g depends only on intramolecular electronic properties. r is the distance between the paramagnetic groups. Measuring the distance-dependence of $J(r)$ yields information on $V^2(r)$.

The most simple model system which yields a distance-dependent exchange interaction are two hydrogen atoms separated in the vacuum beyond a distance r of 5Å, say. HERRING and FLICKER [6] determined

$$J(r) = -7.71 \cdot 10^9 \text{ Gauss } r^{5/2} \exp(-2r/a_0) \quad (3)$$

where r is in Angstrom. In case of the electronic interaction in

the reaction center the protein should modify (3). If one likens the interior of the reaction center to an organic solvent, one may replace (3) by an expression suggested by deKANTER et al. [7] on the basis of CIDNP experiments involving two radicals chained together by polymethylene

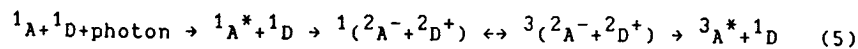
$$J(r) = 9.46 \cdot 10^9 \text{ Gauss} \exp(-2.136r/A) \quad (4)$$

We have pointed out above in discussing the second factor in equation (1) that electron-transfer rates are strongly influenced by nuclear motions. The low-frequency part of this factor stems from the stochastic motion of electron acceptor and donor as well as solvent molecules. The effect of this stochastic motion can also be investigated through the exchange interaction, as demonstrated in [7].

In order to obtain information on $J(r)$ we will analyze recent experiments by WELLER, STAERK and TREICHEL [8] which demonstrated the existence of magnetic field effects on reactions between the paramagnetic end groups of a polymer in an organic solvent. The experiment and the underlying spin dynamics will be explained in Section 2. In Sections 3 we provide a description of the folding motion of polymers. In Sections 4,5 we present an analysis of the experiments in Ref. 8. We show that the observed magnetic field effects can be explained through the folding motion of the polymer. This folding stochastically alters the exchange interaction between the paramagnetic end groups, and thereby affects their spin dynamics. The analysis provides evidence in favour of (4). In Section 6 we discuss this result [9].

2. Spin Pair Dynamics of Biradical Systems

An example of a reaction which is influenced by weak magnetic fields is the light-induced electron-transfer reaction [10,11,12] involving molecules 1A (electron acceptor, here pyrene) and 1D (electron donor, here dimethylaniline) which yield triplet molecules $^3A^*$ according to the scheme



This route to triplets involves the intermediate doublet pair

$^2A^- + ^2D^+$ which is born in an overall singlet state denoted by $^1(2A^- + 2D^+)$. This pure spin state is perturbed by the interactions collected in the Hamiltonian

$$H = H_1 + H_2 + V(J) \quad (6)$$

$$H_i = g\mu_B \cdot \underline{S}_i + \sum_{k=1}^{N_i} a_{ik} \underline{I}_{ik} \cdot \underline{S}_i \quad ; \quad i=1,2 \quad (7)$$

$$V(J) = J(r) \left[\frac{1}{2} + 2\underline{S}_1 \cdot \underline{S}_2 \right] \quad (8)$$

H_i describes the interaction of the electron spin \underline{S}_i of $^2\text{pyrene}^-$ ($i=1$) and $^2\text{dimethylaniline}^+$ ($i=2$) with the external magnetic field \underline{B} (Zeeman interaction) and with the N_i nuclear spins \underline{I}_{ik} (hyperfine interaction). The hyperfine coupling constants assumed for the compounds $^2\text{pyrene}^-$ and $^2\text{dimethylaniline}^+$ are given in Ref. 9. $V(J)$ represents the exchange interaction. The coupling constant J depends on the distance between the paramagnetic molecule as described by (4).

For an observation [10,11] the molecules 1A and 1D are solvated in a polar organic liquid, for example methanol. 1A is excited electronically by a ns laser flash and the formation of $^3A^*$ is monitored by a second light beam. The transient concentration of $^3A^*$ is found to depend strongly on the strength of the external magnetic field \underline{B} . The magnetic field effect can be explained by means of the probability $p_T(t, B)$ that a singlet pair $^1(2A^- + 2D^+)$ assumes triplet character at time t , i.e. reaches the state $^3(2A^- + 2D^+)$. This probability is given by

$$p_T(t, B) = \frac{1}{2} \text{Tr} [Q_T U(t) Q_S] \quad \text{where} \quad (9)$$

$$Q_S = \frac{1}{4} - \underline{S}_1 \cdot \underline{S}_2 = \rho(0) \quad (10)$$

$$Q_T = \frac{3}{4} + \underline{S}_1 \cdot \underline{S}_2 \quad (11)$$

are the projection operators on the singlet and triplet states and $U(t)$ describes the propagator of the density matrix $\rho(t)$ of the system. The trace involves all electron - nuclear spin states and $Z = \text{Tr} Q_S$ is the number of all nuclear spin states. The yield of

triplet products ${}^3A^*$ is then given by

$$\phi_T(B) = \int_0^{\infty} dt \exp(-t/\tau_0) p_T(t, B) \quad (12)$$

where τ_0 is the life time of the doublet pair ${}^2A^- + {}^2D^+$. This observable is shown in Fig. 1a,b for situations with fixed exchange interactions $J(r) = 0$ and $J(r) = 150$ Gauss.

In the case $J = 0$ the triplet yield (12) decreases monotonically with increasing magnetic fields and reaches a constant value for fields $B \gg \Sigma_{ik} a_{ik}$. This behaviour is well understood [13]. In the case of a non-vanishing exchange interaction, the singlet and triplet levels are energetically shifted with respect to each other by $2J$. For $J \gg \Sigma_{ik} a_{ik}$ singlet and triplet transitions cannot be induced by the hyperfine coupling except at fields $B \approx 2J$ when (for $J > 0$) the triplet state T_{-1} becomes degenerate with the singlet state S_0 . This degeneracy causes the maximum of the triplet yield $\phi_T(B)$ in Fig. 1b.

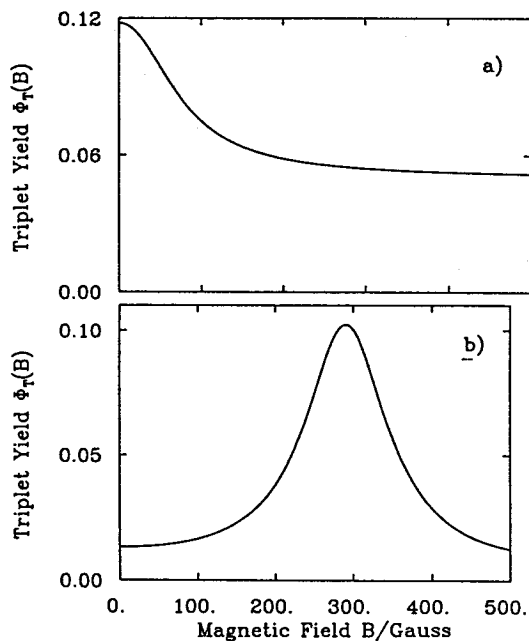


Fig. 1: Magnetic field dependence of the triplet yield $\phi_T(B)$ of a ${}^2(\text{pyrene})^- + {}^2(\text{dimethylaniline})^+$ pair with a life time $\tau_0 = 1$ ns; (a) $J = 0$ Gauss, (b) $2J = 300$ Gauss.

The yield in Fig. 1a for a vanishing exchange interaction agrees well with the observations when 1A and 1D are separate molecules which diffuse freely (except for the Coulomb attraction of the doublet pair) in the solvent. The magnetic field dependence observed in Ref. 8 on polymeric diradical systems exhibits a maximum at intermediate fields and resembles more the yield in Fig. 1b, i.e. is indicative of a non-vanishing exchange interaction.

However, the observations in Ref. 8 also show important differences compared to the yield as shown in Fig. 1b. First, the maximum value of the yield $\phi_T(B_{\text{max}})$ is only about 20 percent larger than the yield $\phi_T(B=0)$ at zero field. Second, the observed maximum is much broader. These features point to the possibility that the doublet pair ${}^2A^-(\text{CH}_2)_n-{}^2D^+$ formed as an intermediate experiences a distribution of exchange interactions. Here we want to demonstrate that this is, in fact, the case. However, the distribution of exchange interactions which explains the observation does not reflect the static folding pattern of the polymer, but rather originates from the dynamics of the folding polymer. The exchange interaction (2) has to be considered a stochastic variable for the doublet pair ${}^2A^-(\text{CH}_2)_n-{}^2D^+$.

3. Computer Simulation of the Polymer Folding

The origin of the stochastic variation of the exchange energy between the paramagnetic end groups of ${}^2A^-(\text{CH}_2)_n-{}^2D^+$ is the folding of its polymer moiety $-(\text{CH}_2)_n-$. The relevant stochastic variable is the distance $r(t)$ between the two polymer ends. In a 'mean field' description the time-dependent distribution of end-end-distances $p(r, t)$ satisfies the Fokker-Planck equation

$$\partial_t p(r, t) = L(r) p(r, t) \quad (13)$$

$$L(r) = D \partial_r p_0(r) \partial_r [p_0(r)]^{-1} \quad (14)$$

Here $p_0(r)$ denotes the equilibrium distribution function of the end-end-distances and D is the effective diffusion coefficient, the value of which should be somewhat smaller than the sum of the diffusion coefficients of the separate groups ${}^2A^-$ and ${}^2D^+$. The static distribution $p_0(r)$ entails information on the steric interactions of the polymer chain $-(\text{CH}_2)_n-$.

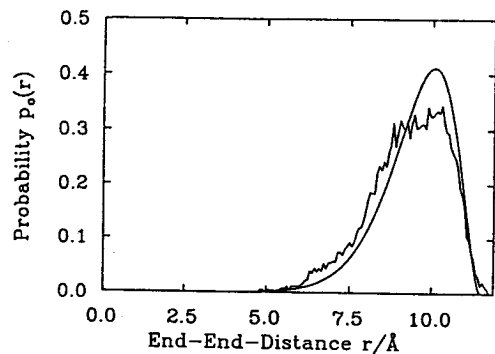


Fig. 2: Distribution of end-end distances for the polymer $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$ resulting from a molecular dynamics calculation involving the computer program of KARPLUS et al. [14]. The hydrogen atoms in this compound were not explicitly described, but only included through an increase of the van der Waals radii of the carbon atoms. These atoms were subjected to random forces and friction. For actual calculations it is convenient to employ a smooth equilibrium distribution $p_0(r)$. Therefore, we approximated the molecular dynamics result by the smooth curve (—).

In lieu of available information on $p_0(r)$ we have generated this distribution by a computer simulation which models the force field between all atoms of the system and integrates the Newtonian equations of motion for all degrees of freedom. The simulation program employed has been developed by KARPLUS and coworkers [14] for the description of the dynamics of biological macromolecules. In our simulation we added random forces and friction to all atoms in order to describe the effect of a solvent. The distribution resulting from sampling the $r(t)$ values of a long-time trajectory of the polymer is presented in Fig. 2.

4. Computer Simulation of the Spin Dynamics

In order to evaluate the propagator $U(t)$ for the density operator in the representation of the electron-nuclear spin states, we employ the von Neumann equation

$$\partial_t \rho = -i H[J(t)] \rho \quad (15)$$

where $H[J(t)] = [H[J(t)], \dots]$. Here $H[J(t)]$ denotes a time-dependent superoperator, $H[J(t)]$ the Hamiltonian (6) and $[,]$ the commutator. The propagator can be formally written

$$U(t) = \langle \exp_{-i} \left\{ -i \int_0^t dt' H[J(t')] \right\} \rangle \quad (16)$$

where $\langle \rangle$ represents the ensemble average over all histories of

$J[r(t)]$ -values when the system assumes initially the distribution of end-end-distances $p_0(r)$. The exponential operator in (16) is time-ordered and is defined by the limit $\epsilon \rightarrow 0$ of

$$\exp(-i\epsilon H[J(N\tau)]) \cdots \exp(-i\epsilon H[J(2\tau)]) \exp(-i\epsilon H[J(\tau)]) \quad (17)$$

with $N\tau$ constant.

The magnetic field dependence of the triplet yield $\phi_T(B)$ resulting [9] for a (pyrene)⁻-(CH₂)_n-(dimethylaniline)⁺ pair of paramagnetic groups with an end-end equilibrium distribution of Fig. 2 is presented in Fig. 3. The yield shown closely resembles the observation of Ref. 8 in that the maximum of $\phi_T(B)$ in Fig. 3 lies at the field $B_{\text{max}} = 300$ Gauss, which compares well with the observation of $B_{\text{max}} = 285$ Gauss. The ratio $\phi_T(B_{\text{max}})/\phi_T(B=0)$ is found theoretically to be 1.1 and experimentally to be 1.3. These latter values have to be compared with a ratio of 5 obtained if a fixed exchange interaction of $2J = 300$ Gauss is assumed (see Fig. 1b). The good agreement with the observation shows that one can explain the magnetic field dependence of the triplet yield $\phi_T(B)$ in polymethylene-linked donor acceptor systems with the stochastic modulation of the distance-dependent exchange interaction (4). This finding argues against an influence of a 'through bond exchange' along the aliphatic chain (which should not be modulated stochastically) and settles the dispute [15] about the origin of the exchange interaction in this polymeric system in favour of an exchange straight through the space (solvent) between the end groups.

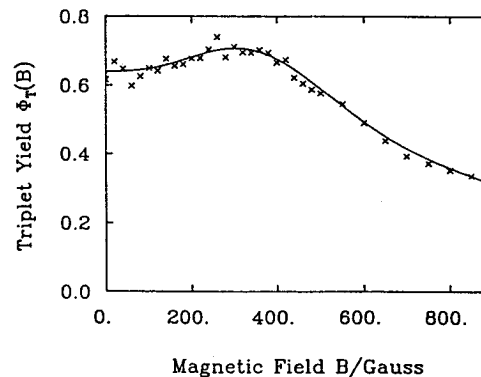


Fig. 3: Magnetic field dependence of the triplet yield $\phi_T(B)$ of the polymeric compound ${}^2(\text{pyrene})^--(\text{CH}_2)_n-{}^2(\text{dimethylaniline})^+$ resulting from the computer simulation of Ref. 9 (+ + +) and resulting from the approximation (19) presented in Sect. 5 (—).

The computer simulation which yielded the results in Fig. 3 is extremely time consuming, and demanded a CPU time of about 100 hrs on a VAX-11/750. This vast amount of computer time is due to the Monte Carlo character of the algorithm [9] which requires large enough samples to produce significant results. The simulation does not yield many insights about the behaviour of the stochastic spin system, e.g. does not provide an answer about the question why the maximum of $\phi_T(B)$ is observed at about 300 Gauss. The computer time of the theoretical description can be drastically reduced and insight can be gained if one employs an approximate description presented in the next Section.

5. Spectrum of the Stochastic Exchange Interaction

In this Section we seek an approximation of the propagator (16). The necessary ensemble average for the fluctuating exchange interaction $J(t)$ can be evaluated formally by means of the stochastic Liouville equation [16]

$$\partial_t U(t) = \{ -iH[J(t)] + L \} U(t) \quad (18)$$

where L denotes the Fokker-Planck operator (14). The approximation introduced by us can be cast into the form

$$U(t) \approx \int_{-\infty}^{\infty} dj q(j) \exp[-itH(j)] \quad (19)$$

where the propagator $U(t)$ with a time-dependent (stochastic) superoperator $H[J(t)]$ is replaced by a superposition of propagators $\exp[-itH(j)]$ with time-independent superoperators $H(j)$. Here $H(j)$ denotes the same superoperator as $H[J(t)]$ except that the stochastic exchange interaction $J(t)$ is replaced by the constant j . $q(j)$ represents the spectrum of the stochastic exchange interactions and is defined by

$$q(j) = \frac{1}{\lambda} \text{Re} \langle [i(2j-2J) - L]^{-1} \rangle \quad (20)$$

Equation (19) implies that the spectrum $q(j)$ can be interpreted as a dynamical distribution of exchange interactions j of the polymer system. This distribution is shown in Fig. 4 for the four cases $D = 0, 4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}, 4 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}, 4 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1}$. The

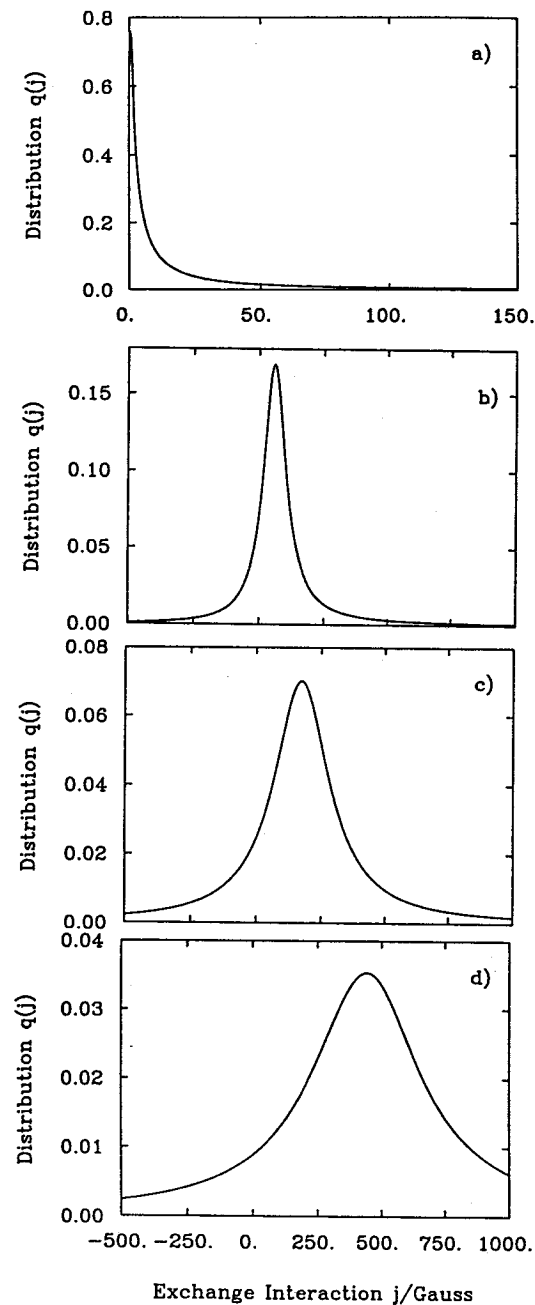


Fig. 4: Spectrum $q(j)$ of the exchange interaction as defined in Eq. (20); (a) for $D=0$; (b) $D=4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; (c) $D=4 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; (d) $D=4 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

different distributions in Fig. 4 show that the folding dynamics shift the spectrum of exchange interactions from small values for $D = 0$ to larger values for increasing D .

The approximation (19) holds exactly for short times, the time scale being defined by the strength of the hyperfine coupling, not the exchange and Zeeman interactions. One can expect that the suggested approximation results in exact triplet yields $\phi_T(B)$ as long as the life time τ_0 is only a few nanoseconds. However, the approximation provides a qualitatively correct magnetic field dependence of $\phi_T(B)$ also for longer life times [28]. The approximation (19) holds exactly for long times in case of either very slow or for very fast stochastic motion of $r(t)$.

Figure 3 compares the magnetic field dependence of the triplet yield $\phi_T(B)$ obtained by means of the approximation (19) with the results from a simulation discussed in Sect. 3. The agreement found is satisfactory. This implies that an interpretation of the observed triplet yield (which also agrees with the curve in Fig. 3) should refer to the spectrum of exchange interactions $q(j)$. The maximum of $\phi_T(B)$ does indeed occur approximately at the field $B_{\max} = 2 j_{\max}$ which corresponds to the maximum $q(j_{\max})$ of $q(j)$ as can be seen from a comparison of Fig. 3 and Fig. 4c. Therefore, the spectrum $q(j)$ relates the magnetic field effect of $\phi_T(B)$ to the folding dynamics of the polymer. The approximation (19) can be employed to study the dependence of $\phi_T(B)$ on the polymer length. The results of such calculations compare well with the available observations [17].

6. Summary

The analysis of the experiments in Ref. 8 show that the spin pair dynamics of polymeric biradicals is influenced by a stochastic folding motion. This folding explores the exchange interaction $J(r)$ between the radical ends. Therefore, the observable, the magnetic field-dependent triplet yield $\phi_T(B)$, is very sensitive to the strength and the distance-dependence of the exchange interaction. The analysis in Sections 4 and 5 revealed that the interaction (4) of de Kanter et. al. describes the observations accurately. One has to conclude that the exchange interactions and electron-transfer rates in the photosynthetic

reaction center, the interior of which should resemble an organic solvent, is governed by a $V^2(r)$ similar to that which underlies (4). The decay constant of (4) is slightly out of the range of $1-2A^{-1}$ as given in Ref. 6.

The discussion above shows very clearly the dominant role which the stochastic dynamics of molecules play on electronic interactions. This should also be the case for the electron transfer in the reaction center. However, in the latter case the description of the stochastic motion is simpler than in case of the folding polymer. The reason is that the polymer folding alters the end-end-distance very drastically, whereas the stochastic motion of the protein atoms extends only a few tenths of an Angstrom from their equilibrium positions [18]. As a result the coupling to a stochastic matrix element $V^2[r(t)]$ can be assumed in the 'motional narrowing' limit.

7. Acknowledgements

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