

On spin-exchange and electron-transfer rates in bacterial photosynthesis

(magnetic field effects/reaction center/bacteriochlorophyll dimer/bacteriopheophytin)

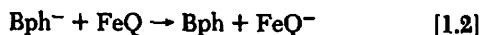
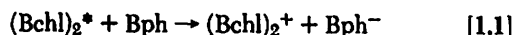
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ABSTRACT A discrepancy is explored regarding the spin exchange integral estimated from magnetic field effects on recombination of the bacteriochlorophyll dimer cation $(\text{Bchl})_2^+$ and the bacteriopheophytin anion Bph^- and the measured electron transfer rate between Bph and electronically excited $(\text{Bchl})_2$. In one explanation considered here there are two sites for the electron or for the hole, with a hopping between sites.

1. INTRODUCTION

A mechanism currently assumed in bacterial photosynthesis (1-6) involves electron transfer between an electronically excited bacteriochlorophyll special pair $(\text{Bchl})_2^*$ and a bacteriopheophytin (Bph), followed by electron transfer to an iron-ubiquinone complex FeQ .



and by subsequent steps. Studies of magnetic field effects on the back reaction (1.3 and 1.4)



in which T denotes a triplet state and $(\text{Bchl})_2$ is the ground state singlet, have led to an estimate of the spin exchange integral for the radical pair in [1.1] and, in turn, to the electron transfer integral for [1.1]. A discrepancy then arises in the calculated compared to the experimental electron transfer rate. There are several possible explanations, one of which is explored in the present paper: There are one $(\text{Bchl})_2$, two Bchls , and two Bphs in the reaction center (1-6). We consider a possible hopping of the electron (or hole) in the $(\text{Bchl})_2^+ \text{Bph}^-$ pair between two sites.

The triplet yield increases from 10 to 20% at room temperature to 100% at 20 K and is also influenced by an external magnetic field (7-9). At room temperature it decreases by about 40% to 2 kG, much of the decrease occurring at the relatively low field of less than 30 G. This magnetic field effect can be understood in terms of singlet-to-triplet transitions in the radical pair $(\text{Bchl})_2^+ \text{Bph}^-$ induced by hyperfine interaction (7-12). The spin exchange integral J is the splitting of the triplet and singlet states of the free radical pair $(\text{Bchl})_2^+ \text{Bph}^-$ and is estimated from magnetic field effects to be, at most, 10^{-3} cm. There are several mechanisms that contribute to J (13). Probably the dominant one is due to a virtual transfer of the electron from the Bph^- to the empty excited orbital in $(\text{Bchl})_2^+$, where it undergoes a strong intramolecular exchange interaction with

the hole. The electron transfer integral ϵ for transfer from $(\text{Bchl})_2^* \text{Bph}$ to $(\text{Bchl})_2^+ \text{Bph}^-$ is then related to J by an expression derived by Anderson (13):

$$J = 2\epsilon^2 J_{\text{int}} / (\Delta E)^2, \quad [1.5]$$

in which ΔE is the vertical energy difference of the $(\text{Bchl})_2^* \text{Bph}$ and $(\text{Bchl})_2^+ \text{Bph}^-$ states and J_{int} is the splitting of the excited singlet and triplet states of $(\text{Bchl})_2$, and is approximately 2500 cm^{-1} (3). The relation [1.5] is similar to one describing virtual transfer into an already half-occupied orbital (13-16). Taking ΔE to be of the order of 3000 cm^{-1} and $J \leq 10^{-3} \text{ cm}^{-1}$, ϵ^2 is of the order of 2 cm^{-2} . We next introduce this value for ϵ^2 into a reaction rate expression. The Fermi Golden Rule expression (17), applied to the rate constant k for electron transfer reaction between two fixed sites, is

$$k = \frac{2\pi\epsilon^2}{\hbar} \sum_{i,f} |\langle \psi_f | \psi_i \rangle|^2 p_i \delta(E_f - E_i), \quad [1.6]$$

in which the overlap integral was factored into an electronic part ϵ and a vibrational part $\langle \psi_f | \psi_i \rangle$ by using the Condon approximation. Eq. 1.6 assumes a continuous distribution of final vibrational states f ; p_i is the probability of finding the reactants in an initial vibrational state i .

Eq. 1.6 can also be written as

$$k = \frac{2\pi\epsilon^2}{\hbar} \frac{1}{\delta E} \sum_{i,f} |\langle \psi_f | \psi_i \rangle|^2 p_i, \quad [1.6a]$$

in which the sum over f is over all states f whose energy E_f lies in the interval $(E_i, E_i + \delta E)$.

If one considers a range of $\delta E = 200 \text{ cm}^{-1}$ (a typical relevant vibration frequency^c, so that at least one state f is in δE) and considers, as a maximum, ψ_i to have an overlap of unity with some final vibrational state f and zero with the others, then from Eq. 1.6,

$$k \leq \frac{2\pi\epsilon^2}{\hbar} \frac{1}{h\nu}. \quad [1.7]$$

This k , with ϵ^2 replaced by 2 cm^{-2} , is calculated thereby to be less than or of the order of 10^{10} sec^{-1} , as compared with the experimental value equal to or exceeding $2 \times 10^{11} \text{ sec}^{-1}$ (19) for reaction 1.1.^d Other models yield analogous results. For example, in a system having all vibration frequencies equal and at low enough temperatures that there is only one initial vibrational state i , the ground state, Eq. 1.6 yields (22-24)

$$k = (2\pi\epsilon^2/\hbar)(1/h\nu) \exp(-a)p/p_i, \quad [1.8]$$

Abbreviations: Bchl , bacteriochlorophyll; Bph , bacteriopheophytin.

^c This frequency was used (18) to model the behavior of the rate constant of a $(\text{Bchl})_2$ -cytochrome c reaction becoming temperature independent at low temperatures.

^d For subtleties of interpretation of the experimental data see refs. 19-21.

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in which a is related to a reduced displacement of the two potential energy surfaces of the reaction (it is $\lambda/h\nu$, using the symbol λ of refs. 24 and 25) and p is a reduced "exothermicity" $-\Delta/h\nu$ ($-\Delta$ is the standard free energy of reaction). The factor multiplying $2\pi\epsilon^2/h$ is less than unity since the sum of $a^p/p!$ over all integers p (0 to ∞) is $\exp(a)$. Thus, the discrepancy is even greater than given by [1.7].

Another model for Eq. 1.6 is the semiclassical model (26, 27); there, $\delta(E_i - E_f)$ is inserted in the integral $\langle\psi_f|\psi_i\rangle$ and replaced by $\delta(V_r - V_p)$, V_r and V_p being the potential energy functions of the reactants and products, respectively, and harmonic oscillator wave functions are used for the ψ_i s. For the case of equal frequencies, one obtains (18)

$$k = (2\pi\epsilon^2/h)(1/h\nu) \frac{\exp[-(\Delta + \lambda)^2/2\lambda h\nu \coth \gamma]}{[2\pi a \coth \gamma]^{1/2}} \quad [1.9]$$

in which $\gamma = h\nu/2kT$. Once again, the factor multiplying $2\pi\epsilon^2/h$ is less than unity, at room temperature, for values of a for which Eq. 1.9 is valid. The same conclusion follows when the classical limit of Eq. 1.9 ($h\nu/2kT \ll 1$) is used.^e

Similar remarks apply to a more general expression obtained from Eq. 1.6, in which both ψ_i and ψ_f are written as harmonic oscillator wave functions, yielding (22, 23, 28)

$$k = (2\pi\epsilon^2/h)(1/h\nu) I_p(a/\sinh \gamma) \exp\left(-\frac{\Delta}{2kT} - a \coth \gamma\right), \quad [1.10]$$

in which I_p is the modified Bessel function. A summation of $I_p(a/\sinh \gamma) \exp(-\Delta/2kT - a \coth \gamma)$ over p from $-\infty$ to ∞ is unity.^f Because each term of the sum is positive, the coefficient of $(2\pi\epsilon^2/h)(1/h\nu)$ in Eq. 1.10 must be less than unity.

One possible explanation of the discrepancy between these calculated and observed values of the k of 1.1 is that the electron in Bph^- or the hole in $(\text{Bchl})_2^+$ reside on several sites, such that there is one pair of adjacent sites that has a large exchange integral for the $\text{Bph}^--(\text{Bchl})_2^+$ interaction and more remote sites that have a very small exchange integral for $\text{Bph}^--(\text{Bchl})_2^+$. When the system exists with the hole and electron pair so separated, we shall call this the "distant state"; it can experience magnetic field effects even at low magnetic field strengths whereas, when the adjacent pair of sites is occupied, which we will term the "close state," the system can undergo the electron transfer in [1.1], [1.3], and [1.4]. The two-state explanation is explored in the next section.

2. THEORY

We consider a spin Hamiltonian H of a pair of radicals having an electron 1 on radical 1 and a hole 2 on radical 2 in an external magnetic field $\mathcal{H}$ (30, 31)

$$H = H_D + J(R)S_1 \cdot S_2, \quad [2.1]$$

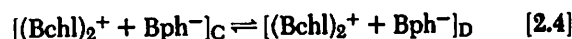
in which

$$H_D = g\beta\mathcal{H} \cdot (S_1 + S_2) + S_1 \cdot \sum_i A_i I_i^{(1)} + S_2 \cdot \sum_m A_m I_m^{(2)}. \quad [2.2]$$

Here, g is the g -factor for a radical, assumed to be the same for each radical $(\text{Bchl})_2^+$ and Bph^- for notational simplicity, β is the Bohr magneton, S_i is the electron (hole) spin vector of the i th radical ($i = 1, 2$), and A_i is the hyperfine interaction constant for interaction of the electron (hole) with the i th nucleus of spin

$I_i^{(i)}$ on the radical i on which that electron (hole) resides ($i = 1, 2$). To simplify the notation, the spin dipolar interaction of the electron with the hole and of each with the nuclei have been neglected in Eqs. 2.1 and 2.2. The second term in Eq. 2.1 is the Heisenberg spin exchange interaction. It depends markedly on the distance R between the radicals. The first term in Eq. 2.2 is the Zeeman energy, and the other two terms represent the magnetic hyperfine interactions.

We consider for brevity a two-state model. In one state C ("close"), the electron and the hole are on radicals adjacent to each other and have a large value of J of $J(R)$. In state D ("distant"), they are on a pair of sites further apart and have $J(R) \approx 0$. For example, state C may be $(\text{Bchl})_2^+$ plus adjacent Bph^- (or adjacent Bchl^-), and state D may be $(\text{Bchl})_2^+$ plus distant Bph^- . In the former case the mechanism of [1.1] now is



i.e., the formation of state C is followed by a hopping motion of the electron on Bph^- to sites that are no longer adjacent. Or, one may have $(\text{Bchl})_2^* + \text{Bchl}^- \rightarrow [(\text{Bchl})_2^+ + \text{Bchl}^-]_C$, which transfers an electron to Bph to yield $[(\text{Bchl})_2^+ + \text{Bph}^-]_D$. Similar remarks would apply to the mechanism of [1.3] and [1.4].

To simplify the discussion, we shall suppose that in state C the spin-exchange interaction $J S_1 \cdot S_2$ is the dominant term in Eq. 2.1; i.e., the spin-Hamiltonian is then H_C ,

$$H_C = J S_1 \cdot S_2. \quad [2.5]$$

We shall assume that in state D the term H_D given by Eq. 2.2 contains the significant contributions to the spin-Hamiltonian; i.e., that $J(R)$ is negligible in state D.^g

We introduce rate constants k_S and k_T for reactions [1.3] and [1.4] when the radical pair is in state C, and zero otherwise. The hopping rate constant for $C \rightarrow D$ will be written as k_C , and for $D \rightarrow C$ as k_D . If the distribution among the sites is statistical, then k_C/k_D would be about 1 when there is one site for C and one for D.

The population of spins in states C and D can be described quantum mechanically by time-dependent quantum mechanical density operators ρ_C and ρ_D . Their equations of motion are familiar from the theory of chemical exchange in spin resonance (32, 33) and are given by (setting $\hbar = 1$ in the following)

$$\frac{d\rho_D}{dt} = -i[H_D, \rho_D] - k_D\rho_D + k_C\rho_C \quad [2.6]$$

$$\frac{d\rho_C}{dt} = -i[H_C, \rho_C] - k_C\rho_C + k_D\rho_D - k_S P^S \rho_C P^S - k_T P^T \rho_C P^T - k_2 (P^T \rho_C P^S + P^S \rho_C P^T), \quad [2.7]$$

in which P^S is the projection operator onto the singlet manifold for the radical pair. P^T is the corresponding operator onto the triplet manifold, so that the trace (tr) of $P^S \rho_C P^S$ and of $P^T \rho_C P^T$ denotes the probability of the radical pair in state C being in a singlet state and in a triplet state, respectively. ρ_D has a similar property for state D. Thereby, the trace of the $k_S P^S \rho_C P^S$ term in Eq. 2.7 represents the rate of formation of a singlet state of $[(\text{Bchl})_2^+ + \text{Bph}]$, and $k_T \text{tr}(P^T \rho_C P^T)$ is the corresponding rate of formation of the triplet state $[(\text{Bchl})_2^{*T} + \text{Bph}]$. The last term in Eq. 2.7 accounts for the disappearance of the off-diagonal

^e One uses equation 25 of ref. 24.

^f E.g., one uses equations 10, 25, and 35 of pp. 5–9 of ref. 29 and a suitable change of variable.

^g The explicit form of H_D is not used in the derivation that follows. Even if, instead of hyperfine terms, some other interaction would induce the singlet-triplet transitions, the conclusions would not be changed.

element of the ρ_C operator (in a singlet-triplet representation). k_2 is equal to or greater than its minimum value $\frac{1}{2}(k_S + k_T)$ (34), and exceeds the latter when spin-dephasing interactions can occur.

We consider a reaction center illuminated by a pulse of light, as in the usual experiments. A reaction that absorbs a photon produces a final yield ϕ_T of triplet states per photon, obtained by an integration

$$\phi_T = k_T \int_0^\infty \text{tr}(P^T \rho_C(t) P^T) dt = k_T \text{tr}(P^T \bar{\rho}_C P^T), \quad [2.8]$$

where $\bar{\rho}_C$ denotes

$$\bar{\rho}_C = \int_0^\infty \rho_C(t) dt. \quad [2.9]$$

Similar remarks apply to ϕ_S , which equals thereby $k_S \text{tr}(P^S \bar{\rho}_C P^S)$.

Equations for $\bar{\rho}_C$ and $\bar{\rho}_D$ can be obtained by integrating Eqs. 2.6 and 2.7 from $t = 0$ to $t = \infty$. The resulting equations are treated in the *Appendix*, by using methods (35, 36) originally developed in the theory of electron spin resonance line broadening due to Heisenberg spin exchange (35). They are shown in the *Appendix* to be equivalent to the equation for the $\bar{\rho}$ arising from the solution of the following one-state equation containing effective constants J^{eff} , k_S^{eff} , k_T^{eff} , and k_2^{eff} :

$$\begin{aligned} \frac{d\rho}{dt} = & -i[H^{\text{eff}}, \rho] - k_S^{\text{eff}} P^S \rho P^S - k_T^{\text{eff}} P^T \rho P^T \\ & - k_2^{\text{eff}} (P^T \rho P^S + P^S \rho P^T) \end{aligned} \quad [2.10]$$

Here, H^{eff} is given by the sum of H_D in Eq. 2.2 and H_C in Eq. 2.5, with the A s and J replaced by A^{eff} s and J^{eff} . $\bar{\rho}$ equals $\int_0^\infty \rho(t) dt$.

The relation of these effective constants to the actual ones in Eqs. 2.6 and 2.7 is shown in the *Appendix* to be given by Eqs. 2.11–2.14 for a set of initial conditions appropriate for an initial electron transfer [1.1] to the close site:

$$k_S^{\text{eff}} = k_S k_D / (k_C + k_S) \quad [2.11]$$

$$k_T^{\text{eff}} = k_T k_D / (k_C + k_T) \quad [2.12]$$

$$J^{\text{eff}} = J k_C k_D / [J^2 + (k_C + k_2)^2] \quad [2.13]$$

$$k_2^{\text{eff}} = k_D [J^2 + k_2(k_C + k_2)] / [J^2 + (k_C + k_2)^2]. \quad [2.14]$$

Expressed in terms of these effective quantities, the triplet yield is given by

$$\phi_T = k_T^{\text{eff}} \text{tr}(P^T \bar{\rho} P^T). \quad [2.15]$$

If the effective one-state model described by Eqs. 2.10–2.14 is fitted to experimental data and if the effective parameter J^{eff} was interpreted as the real one, a discrepancy in the value of k calculated from [1.5]–[1.7] could result. Let us suppose that $\frac{1}{2}(k_S + k_T)$ is of the order of 10^8 sec^{-1} (corresponding to a lifetime of the order of 10 nsec) and that k_C and k_2 are smaller than J . Then

$$J^{\text{eff}} \cong J(k_C/J)(k_D/J). \quad [2.16]$$

Thus, if the geometric mean $(k_C k_D)^{1/2}$ of the hopping rate constants is about 10^9 sec^{-1} and if J is about 1 cm^{-1} (i.e., about $3 \times 10^{10} \text{ sec}^{-1}$), J^{eff} is about 10^{-3} cm^{-1} . Accordingly, the small observed value of J^{eff} ($\leq 10^{-3} \text{ cm}^{-1}$) can be consistent with a much larger J for spin exchange between adjacent sites. A J of 1 cm^{-1} and the values of J_{int} , ΔE , and $h\nu$ cited after Eq. 1.5 would correspond to an ϵ^2 of about 2000 cm^{-2} and to a maximum rate constant of [1.1] of 10^{13} sec^{-1} instead of 10^{10} sec^{-1} .

DISCUSSION

The latter equations of Section 2 admit the following interpretation. The k_S^{eff} in Eq. 2.11 equals the rate constant for the formation of S from D in the sequence,



in which a steady-state assumption is used for C. This k_S^{eff} then equals k_D when $D \rightarrow C$ is the slow step and equals k_S times an equilibrium constant (k_D/k_C) for the ratio C/D when $C \rightarrow S$ is the slow step. Similar remarks apply to Eq. 2.12. Eq. 2.16 for J^{eff} has a certain analogy to a linewidth result in magnetic resonance for a spin hopping (rate constant k) between two sites differing in energy by Δ (35, 37). In the limit of a slow hopping rate ($k \ll \Delta$) between two sites there are two distinct resonance lines in an electron spin resonance spectrum. If one observes one of them, the result of the hopping motion results in (i) a line shift k^2/Δ , which is analogous to the $k_C k_D/J$, and (ii) a lifetime broadening of the electron spin resonance line proportional to k . In our system the analog to two resonance lines is the singlet-triplet splitting in state C ($= J$) and that in state D ($= 0$) and the fact that the hopping motion causes each of the splittings to broaden a little, and to be shifted, by an amount that changes the effective J_D from 0 to $k_C k_D/J$.

We have seen above that the formal equations for the density operator yield the same final expressions for the triplet yield, regardless of whether there are two states, C and D, or only one state, but that the meaning of the coefficients differs in the two cases. The transient behavior on the other hand cannot be identical. In one case one has, in fact, a single first-order differential equation for the density operator while in the other case one has two first-order equations which can be combined to yield a second equation for ρ_C or ρ_D . In principle, thereby, the transient behavior might serve ultimately to distinguish the postulated two-state behavior from the behavior of a single state.

The assumption that electron transfer between $(\text{Bchl})_2$ and Bph proceeds by two steps is supported by recent results (38–40) on photosynthetic reaction centers and is also reminiscent of a hopping mechanism in a quite different system (41).

APPENDIX

Integration of the one-state equation, Eq. 2.10, from $t = 0$ to $t = \infty$, with initial condition $\rho(t = 0) = \rho^0$, yields

$$\begin{aligned} -\rho^0 = & -i[H^{\text{eff}}, \bar{\rho}] - k_S^{\text{eff}} P^S \bar{\rho} P^S - k_T^{\text{eff}} P^T \bar{\rho} P^T \\ & - k_2^{\text{eff}} (P^T \bar{\rho} P^S + P^S \bar{\rho} P^T). \end{aligned} \quad [A.1]$$

We show that Eqs. 2.6 and 2.7 can be made to yield an equation of the above form for $\bar{\rho}$, and comparison of that result with Eq. A-1 then yields equations for the quantities k_S^{eff} , k_T^{eff} , A^{eff} , J^{eff} , and k_2^{eff} .

Eqs. 2.6 and 2.7 are integrated from $t = 0$ to ∞ , for simplicity with initial conditions $\rho_C(t = 0) = \rho_C^0$ and $\rho_D(t = 0) = 0$ (i.e., it is supposed that the electron is first transferred to the close site). One obtains

$$0 = -i[H_D, \bar{\rho}_D] - k_D \bar{\rho}_D + k_C \bar{\rho}_C. \quad [A.2]$$

$$\begin{aligned} -\rho_C^0 = & -i[H_C, \bar{\rho}_C] - k_C \bar{\rho}_C + k_D \bar{\rho}_D - k_S P^S \bar{\rho}_C P^S \\ & - k_T P^T \bar{\rho}_C P^T - k_2 (P^S \bar{\rho}_C P^T + P^T \bar{\rho}_C P^S). \end{aligned} \quad [A.3]$$

Eq. A.3 can be written as an operator $\mathcal{R}$ acting on $\bar{\rho}_C$, plus $k_D \bar{\rho}_D$

$$-\rho_C^0 = -\mathcal{R} \bar{\rho}_C + k_D \bar{\rho}_D, \quad [A.4]$$

in which comparison of Eqs. A.3 and A.4 defines $\mathcal{R}$. Thus, $\bar{\rho}_C$

equals $\mathcal{R}^{-1}(k_D \bar{\rho}_D + \rho_C^0)$. Introducing this result into Eq. A.2 we have

$$-k_C \mathcal{R}^{-1} \rho_C^0 = -i[H_D, \bar{\rho}_D] - k_D \bar{\rho}_D + k_C k_D \mathcal{R}^{-1} \bar{\rho}_D. \quad [\text{A.5}]$$

To show that this equation is equivalent to Eq. A.1 we introduce an ansatz for $\mathcal{R}^{-1}$ and determine the coefficients in the result. Namely, we set (35, 36)

$$-k_D(I - k_C \mathcal{R}^{-1}) \bar{\rho}_D = -i[H_{\text{ex}}^{\text{eff}}, \bar{\rho}_D] - k_S^{\text{eff}} P^S \bar{\rho}_D P^S - k_T^{\text{eff}} P^T \bar{\rho}_D P^T - k_2^{\text{eff}} (P^T \bar{\rho}_D P^S + P^S \bar{\rho}_D P^T), \quad [\text{A.6}]$$

in which I is the identity operator, $H_{\text{ex}}^{\text{eff}}$ is an effective Heisenberg spin exchange operator as in Eq. 2.5 with J replaced by J^{eff} . The H^{eff} in Eq. 2.10 equals $H_D + H_{\text{ex}}^{\text{eff}}$. Therefore, as a first result, $A_i^{\text{eff}} = A_i$. One then operates on both sides of Eq. A.6 by $\mathcal{R}$ (defined via Eqs. A.3 and A.4), obtaining the coefficients J^{eff} , k_S^{eff} , etc., using the properties of P^S and P^T ($= I - P^S$):

$$(P^S)^2 = P^S, (P^T)^2 = P^T, P^S P^T = P^T P^S = 0, \quad [\text{A.7}]$$

and

$$S_1 \cdot S_2 = P^T - \frac{3}{4} I. \quad [\text{A.8}]$$

Eq. A.8 is obtained by noting that $P^T = \frac{1}{2} S^2$ (as can be verified by its action on a triplet state where $S = 1$ and on a singlet state where $S = 0$) and that $S^2 = (S_1 + S_2)^2 = S_1^2 + S_2^2 + 2(S_1 \cdot S_2)$. However, $S_1^2 = S_2^2 = 3/4 I$, and so Eq. A.8 follows. The radical pair is created in a singlet state; thus $\rho_C^0 = P^S / \text{tr } P^S$. The left-hand side of Eq. A.5 is then readily evaluated, by using $\mathcal{R}^{-1}$ as defined in Eq. A.6, and yields $\rho^0 = [k_C / (k_C + k_S)] \rho_C^0$. The ratio of the rate constants arises from the competition of rates involving k_C and k_S in [3.1]. The ratio affects the absolute value of ϕ_T but not its relative dependence on H .

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- Blankenship, R. E. & Parson, W. W. (1978) *Annu. Rev. Biochem.* **47**, 635-653.
- Dutton, P. L., Leigh, J. S., Jr., Prince, R. C. & Tiede, M. (1979) in *Dahlem Workshop on Light-Induced Charge Separation at Interfaces in Biological and Chemical Systems*, eds. Gerischer, H. & Katz, J. J. (Dahlem Konferenzen, Berlin), in press.
- Clayton, R. K. & Sistrom, W. R., eds. (1978) *The Photosynthetic Bacteria* (Plenum, New York).
- Feher, G. & Okamura, M. Y. (1976) *Brookhaven Symp. Biol.* **28**, 183-194.
- Katz, J. J., Norris, J. R., Shipman, L. L., Thurnauer, M. C. & Wasielewski, M. R. (1978) *Annu. Rev. Biophys. Bioeng.* **7**, 393-434.
- Kaufmann, K. J. (1979) *CRC Crit. Rev. Solid State Mater. Sci.* **8**, 265-316.
- Blankenship, R. E., Schaafsma, T. J. & Parson, W. W. (1977) *Biochim. Biophys. Acta* **461**, 297-305.
- Hoff, A. J., Rademaker, H., van Grondelle, R. & Doysens, L. W. M. (1977) *Biochim. Biophys. Acta* **460**, 547-554.
- Michel-Beyerle, M. E., Scheer, H., Seidlitz, H., Tempus, D. & Haberkorn, R. (1979) *FEBS Lett.* **100**, 9-12.

- Haberkorn, R. & Michel-Beyerle, M. E. (1977) *FEBS Lett.* **75**, 5-7.
- Werner, H. J., Schulten, K. & Weller, A. (1978) *Biochim. Biophys. Acta* **502**, 255-268.
- Haberkorn, R. & Michel-Beyerle, M. E. (1979) *Biophys. J.* **26**, 489-498.
- Anderson, P. W. (1959) *Phys. Rev.* **115**, 2-13.
- Hopfield, J. J. (1977) in *Electrical Phenomena at the Biological Membrane Level*, ed. Roux, E. (Elsevier, Amsterdam), pp. 477-492.
- Okamura, M. Y., Fredkin, D. R., Isaacson, R. A. & Feher, G. (1979) in *Tunneling in Chemical and Biological Systems*, eds. Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R. & Sutin, N. (Academic, New York), pp. 109-127.
- Okamura, M. Y., Isaacson, R. A. & Feher, G. (1979) *Biochim. Biophys. Acta* **546**, 394-417.
- Baym, G. (1969) *Lectures on Quantum Mechanics* (Benjamin, New York), Eqs. 12-22-12-23.
- Hopfield, J. J. (1974) *Proc. Natl. Acad. Sci. USA* **71**, 3640-3644.
- Moscowitz, E. & Malley, M. M. (1978) *Photochem. Photobiol.* **27**, 55-59.
- Parson, W. W., Schenck, C. C., Blankenship, R. E., Holten, D., Windsor, M. W. & Shank, C. V. (1978) in *Frontiers of Biological Energetics*, eds. Dutton, P. L., Scarpa, A. & Leigh, J. L. (Academic, New York), Vol. 1, pp. 37-44.
- Mauzerall, D. (1979) *Photochem. Photobiol.* **29**, 169-170.
- Levich, V. G. & Dogonadze, R. R. (1961) *Collect. Czech. Chem. Commun.* **26**, 193-214. (English translation: Boskko, O., University of Ottawa, Canada).
- Levich, V. G. (1966) *Adv. Electrochem. Electrochem. Eng.* **4**, 249-371.
- Marcus, R. A. (1979) in *Dahlem Workshop on Light-Induced Charge Separation at Interfaces in Biological and Chemical Systems*, eds. Gerischer, H. & Katz, J. J. (Dahlem Konferenzen, Berlin), in press.
- Marcus, R. A. (1964) *Annu. Rev. Phys. Chem.* **15**, 155-196.
- Lax, M. (1952) *J. Chem. Phys.* **20**, 1752-1760.
- Schmidt, P. P. (1975) *Theor. Chim. Acta* **40**, 263-270.
- Jortner, J. (1976) *J. Chem. Phys.* **64**, 4860-4867.
- Bateman, H. (1953) *Higher Transcendental Functions* (McGraw-Hill, New York), Vol. 2.
- Kaptein, R. (1972) *J. Am. Chem. Soc.* **94**, 6251-6262.
- Closs, G. (1974) *Adv. Magn. Reson.* **7**, 157-229.
- Kaplan, J. (1958) *J. Chem. Phys.* **28**, 278-282.
- McConnell, H. M. (1958) *J. Chem. Phys.* **28**, 430-431.
- Sargent, M., Scully, M. D. & Lamb, W. E., Jr. (1974) *Laser Physics* (Addison-Wesley, Reading, MA), Eq. 37.
- Eastman, M. P., Kooser, R. G., Das, M. R. & Freed, J. H. (1969) *J. Chem. Phys.* **51**, 2690-2709.
- Haberkorn, R. (1977) *Chem. Phys.* **19**, 165-179.
- Carrington, A. & McLachlan, A. D. (1967) *Introduction to Magnetic Resonance* (Harper & Row, New York).
- Shuvalov, V. A., Klevanik, A. V., Sharkov, A. V., Matveetz, Lu. A. & Krukov, P. G. (1978) *FEBS Lett.* **91**, 135-139.
- Shuvalov, V. A. & Asadov, A. A. (1979) *Biochim. Biophys. Acta* **545**, 296-308.
- Palliotin, G., Vermeglio, A. & Breton, J. (1979) *Biochim. Biophys. Acta* **545**, 249-264.
- Bube, W., Michel-Beyerle, M. E., Haberkorn, R. & Steffens, E. (1977) *Chem. Phys. Lett.* **50**, 389-393.