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Activationless electron transfer in the reaction centre of photosynthesis

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The reorganization energies of the medium and the activation energies of electron transfer in the photosynthetic reaction centre have been calculated (the geometric parameters are assumed in accordance with the X-ray crystallographic analysis data for *Rhodopseudomonas viridis*). Due to the low reorganization energy of the protein medium and the optimum relations of the effective dimensions of reagents, for each step of the main electron transfer path, the corresponding reorganization energy and the free energy of reaction (difference of redox potentials) are similar. As a result, the activation energy of each of these electron transfer steps is negligible. The electron back-transfer from the primary acceptor to the primary donor, though strongly advantageous thermodynamically, is hindered by high activation energy.

Primary charge separation in the photosynthetic reaction centre (RC) and further electron transfer to the acceptor, quinone, are very fast processes. These reactions have been reliably proved to be practically activationless [1]. Their activationless nature was also assumed in a theoretical analysis of the processes at the reaction centre [2–6]. The physical reasons, however, for the practically zero activation energy for these different processes characterized by essentially different energy changes are still not quite clear. Except for one quite recent paper [7], which will be discussed below, there have been no attempts to evaluate the activation energy theoretically. Usually, one adjusts the total reorganization energy, E_r, to the experimental value of the free energy of the elementary act, ΔI ($E_r \simeq -\Delta I$), to obtain activation energy $E^{\ddagger} \simeq 0$ (see below, Eqn. 1).

As was correctly pointed out in Ref. 1, due to delocalization of the charge in the extended π-system, the changes in chlorophyll molecules during their oxidation or reduction should not be large. The estimates of the reorganization energy of molecules based on the data on the differences in the structure of quinone and semiquinone molecules obtained in Ref. 8 give values of the order of 0.04 eV. For chlorophylls, with their much greater delocalization of electrons, a still lower internal reorganization energy would be expected.

Charge transfer is inevitably bound up with reorganization of the surrounding dielectric, with a change in its polarization. The concept of the significant contribution of the reorganization of the medium to the activation energy is one of the main premises of the modern theory of charge transfer reactions (see, for example, Refs. 9, 10). In a harmonic approximation, the activation energy, $E^{\ddagger}$, is determined by the expression

$$E^{\ddagger} = \frac{(E_r + \Delta I)^2}{4E_r} \quad (1)$$

The total reorganization energy, E_r, equals to the sum of the reorganization energies of the medium, E_s, and the intramolecular reorganization energy, E_i. The latter can be calculated on the basis of experimental data on the changes of bond lengths and angles during the reaction and on corresponding vibrational frequences. As mentioned before, in the case of interest E_i is supposed to be small.

For the medium reorganization energy in protein systems, two different but in a sense complementary approaches are now in use. The first one advanced by Warshel (see, for example, Refs. 11–13), is purely microscopic. Warshel has developed a method of self-con-

Abbreviations: BChl, bacteriochlorophyll (a single molecule), $(BChl)_2$, special pair; (BChl), bacteriochlorophyll molecule in the special pair, BPheo, bacteriopheophytin; Q, quinone; MQ, menaquinone; RC, reaction centre.

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sistent iterative calculations of charge–dipole (partial charges) interactions and the method of an adiabatic 'charging' of the reactants which permits us to evaluate both E_s and the contribution to ΔI caused by the charge–medium interaction. Due to the great complexity of the system, this approach, very attractive in principle, has to resort in its practical implementation to several simplifications and assumptions. In spite of those, however, it gives reasonable results. The primary charge separation in RC has been analysed in a framework of this method in Ref. 7.

The other approach presenting a combination of continual and microscopic description was developed in our works on enzyme kinetics (for review see Refs. 14–16). In this method the process of protein reorganization, i.e., small shifts and turns of polar, mainly peptide, groups, is described in an averaged way as a continual dielectric response (if necessary, the heterogeneity of medium is taken into account). At the same time, the charge–medium interaction component of ΔI is calculated on the basis of the protein microstructure because the energy of ionized groups inside the protein depends substantially on the intraglobular electric field.

The latter is determined by the orientation of the protein dipoles fixed in a definite structure and is almost independent of the charge of reactants. The ion's 'solvation energy' (and hence ΔI) inside the protein depends on the point of the reactant's localization and on the sign and magnitude of its charge. Let us assume now that, after the charge transfer, only small changes of the protein structure occur (evidently, some exceptions are possible – see, for example, Ref. 11). That means the changes in protein polarization which are responsible for the reorganization energy can be described in a continual way. In the framework of this dielectric formalism, E_s is proportional to e^2 (where e is not the total charge but the charge being transferred), and hence is independent of the sign and the absolute values of reactant charges [9,10]. This approach also proves to be in a semiquantitative agreement with the experiment.

In this paper, I will apply my approach to various charge transfer reactions in RC. I will restrict myself to the calculation of E_s, and for ΔI the experimental values rather than calculated ones will be used with the aim of ensuring a higher accuracy of results.

The value of E_s is determined by the contribution of the reorganization of the slow classical subsystem equal to the difference of the contributions of the total and the electronic, practically inertialess, polarizations. This difference is proportional to the quantity $C = 1/\epsilon_o - 1/\epsilon_s$, where ϵ_o and ϵ_s are the optical (electronic) and static dielectric constants. Since the total polarization includes the contribution of the highest-frequency infrared vibrations, which are of quantum nature already at room temperature and therefore do not affect the reorganization of the classical subsystem, the quantity C actually enters into the expression for E_s with a certain coefficient of less than unity. From the experimental data on the frequency dependence of dielectric permittivity, this coefficient for water was found to be about 0.8 [17].

In discussing the situation for a protein medium, for a reaction centre in particular, we have to deal with the fact that part of protein polarization associated with the changes in the orientation of its large-scale structural units may prove to be too slow to participate in very fast electron transfer processes (the possibility of an insufficiently fast relaxation of nuclei, but as applied to intramolecular reorganization, was discussed in Ref. 2). Then the corresponding contribution should not be taken into account in E_s. But in that case the value of ΔI must correspond to a certain nonequilibrium polarization of the surroundings and cannot be determined directly from the experimental data on the equilibrium redox potentials of components.

It seems to me, however, that some uncertainties associated with this cannot introduce a large error into the results of the calculation. The point is that for large-scale structural units the corresponding part of the polarization is characterized by a large space correlation radius [18]. In the nonlocal electrostatics theory [19], the effect of the space correlation is taken into account; this means, the effect of the correlation of polarization in two different point in the medium. In the case where the distance between these points is smaller than some length, λ, characteristic of the medium (correlation radius), the polarization at one point depends on the polarization at other, irrespective of the electric field at the first point. Different kinds of polarization – orientational, atomic, electronic – have different characteristic radii, λ, λ for the first type being the largest. It is highly probable that, for proteins, a major part of the orientational polarization due to turns and bends of the polypeptide backbone is characterized by a very large λ_{or}, reflecting the highly organized macromolecular structure. The contribution of this polarization into ion-dielectric interaction energy is proportional to $(1/\epsilon_* - 1/\epsilon_s)$, where ϵ_s describes the total polarization and ϵ_* corresponds to effects caused by all weakly correlated kinds of polarization (electronic, atomic; possibly orientational of some side-chains). If this radius is much larger than the radii of reagents, r, then, in keeping with the theory of media with space correlation [19], the quantity $(1/\epsilon_* - 1/\epsilon_s)$ will figure in a first approximation in the equations for the reorganization energy and for Born's solvation energy with a coefficient close to $1/\lambda_{or}$ instead of $1/r$, i.e., it will make a contribution about λ_{or}/r times less than in a theory which does not take into account the space correlation. For proteins, the quantity ϵ_*, i.e., the high-frequency limit of the dielectric permittivity corresponding to the strongly cor-

related orientational polarization, should not be less than the infrared permittivity (ϵ_{ir}) for liquid amides which are not characterized by a large-scale polarization correlation. For proteins ϵ_s is estimated at 4 and ϵ_{ir} for amides is about 3.5, and at $\lambda_{or}/r = 2$–3, the corresponding contribution is 0.012 to 0.018. This value is small compared to $C \simeq 0.15$ to 0.20, and therefore the error introduced by its incomplete effect upon the reorganization energy may be ignored. The corresponding contribution to the equilibrium energy difference is about 0.03 eV and its deviation from the equilibrium value lies within the error of an experimental determination of the difference of redox potentials.

The value of ϵ_o for proteins should not differ significantly from that for amides, i.e., 2.1 to 2.2. Taking into consideration the above reasoning, it would be more correct to choose for ϵ_s a value close to 3.5. In addition, we must take into account the quantum nature of a part of infrared polarization (vibrations of N–H bonds, etc) somewhat decreasing the reorganization energy. All these factors give the estimate of the effective value $C_{eff} = 0.15$. The error in the estimation of this value (and hence of E_s) can be evaluated as ± 20–30%.

The question may be posed as to whether it is justifiable to describe in a continual approximation the reorganization of the reactants' closest neighbours or whether this process should be treated on a microscopic level like the intramolecular reorganization. We have no direct X-ray crystallographic data demonstrating the change of coordinates of the protein's groups adjacent the reactants due to a charge transfer. Some marked shifts of protein's side-chains were observed in cytochrome *c* reduction, and the contribution of these shifts into reorganization energy was calculated microscopically by Churg et al. [11] as being equal to about 0.1 eV. This figure is close to the contribution to reorganization energy due to the layer of approx. 2–2.5 Å thickness surrounding the reactants, i.e., a layer a little bit thicker than a layer of atoms in a closest van der Vaals contact (calculated by Eqn. 2, see below). Hence, we can estimate the possible error due to a continual approximation by few hundredths of an electron-volt.

The reaction centre is situated in the membrane, some of its components being quite close to the membrane surface. However, we do not take into account the interaction of the charge with the aqueous phase since, as shown by X-ray diffraction data [20,21], the special pair $(BChl)_2$ is well screened from water by nonhelical parts of proteins L and M (and partly by cytochrome bound with RC), and menaquinone located near the other side of the membrane is screened by the protein H. As shown by our previous calculations [18,22], when the charges are localized at such depth the influence of the water environment on the reorganization energy is negligible.

The shape of the reagents – chlorophylls, quinones – is far from spherical; it is roughly that of oblate ellipsoids. For the molecules of BChl, BPheo and quinone, Q (and to a somewhat lesser extent for menaquinone, MQ), the ellipsoid parameters can be fairly well estimated by means of molecular models (see Table I). The description of the special pair $(BChl)_2$ as an ellipsoid is more approximate, the estimation of its parameters is based on the model of the arrangement of two BChl molecules in a pair (according to the data of [20]), the centre of the ellipsoid is located in the middle of the line connecting the Mg atoms of the two molecules of the pair. Since, however, the term related to the dimensions of $(BChl)_2$ makes the least contribution to the value of E_s, the latter proves to be little affected by the error in the determination of the corresponding parameters (see below).

In describing the electron transfer from the special pair, the question arises as to the character of the charge delocalization. For this reason I carried out a calculation for two extreme assumptions: the charge is delocalized equally on both molecules (in this case we denote the reagents as $(BChl)_2$) and the charge is distributed only on one of them, which is nearer to the transfer chain (we denote it as (BChl)).

Due to delocalization of the charge over the whole reagent molecule, the conducting ('metal') ellipsoids model is suitable for calculating E_s. As shown in Ref. 23, in this case the result can be expressed by an equation similar to Marcus' equation

$$E_s = e^2 C_{eff}\left(\frac{1}{2r_{eff1}} + \frac{1}{2r_{eff2}} - \frac{K}{R}\right) \qquad (2)$$

where e is the charge being transferred, R is the distance between the centres of reagent molecules, and the effective radii are expressed in terms of the ellipsoid semiaxes as follows:

$$r_{eff} = \frac{\sqrt{a^2 - c^2}}{F(k,\phi)}$$

Here, $F(k, \phi)$ is the elliptic integral of the first kind, whose parameters are $k = \sin\alpha = \sqrt{(a^2 - b^2)/(a^2 - c^2)}$ and $\phi = \arcsin\sqrt{(a^2 - c^2)/a^2}$. As seen from

TABLE I

Geometric parameters of reagents, Å

Reagent	Ellipsoid semiaxes			Mean radius	Effective radius
	a	*b*	*c*	r_{av}	r_{eff}
BChl, BPheo	7.65	7.65	1.8	5.70	5.56
$(BChl)_2$	10	7.65	3.3	6.99	6.89
MQ	3.65	3.25	1.7	2.86	2.84
Q	3.95	2.4	1.7	2.68	2.66

Table I, the values of r_{eff} thus calculated are only a little less than that of r_{av} – the arithmetic mean of three semiaxes – this difference increasing with the ellipsoid nonsphericity.

The coefficient K is close to unity and, for the case of two similar ellipsoids, is expressed as a series whose most important terms are equal to $\{1+[(2a^2-b^2-c^2)/3R^2]+[(abc)/3R^3]\}$. It has this form when the line connecting the centres of the ellipsoids coincides with their major semiaxes a. In this case for the two nearest BChl (or BPheo) molecules $K=1.18$. If, however, the minor semiaxes, c, lie on this line, then the substitution $a \rightleftarrows c$ must be made and the coefficient will be equal to 0.73. In the RC the planes of the (BChl) and BChl molecule and those of BChl and BPheo molecules lie at the angles of 64° and 70° [20], i.e., their orientation is intermediate between the two orientations described above and, therefore, the correction factor can be estimated at $K \gtrsim 0.9$ (the exact solution for an arbitrary mutual orientation of ellipsoids is not known). The introduction of this correction increases the reorganization energy by no more than about 10%. For other pairs of reagents, the corresponding effect is much less. Considering the small value (and low accuracy of the calculation) of the correction terms, in the following I have assumed $K=1$.

The results of the calculation of the reorganization energy E_s by Eqn. 2 are listed in Table II. The values of E_s are given up to the second significant digit, which does not represent the actual accuracy of calculation. They are presented in this form to make more clear the small changes of E_s in going from one pair of reagents to another. In calculations of $E^{\ddagger}$ for the reactions of quinones (see below), account is taken not only of E_s but also of the intramolecular reorganization energy, E_i.

It is expedient to stress here that for three possible reactions of primary charge separations ($(BChl)_2^* \rightarrow$ BChl, $(BChl)_2^* \rightarrow$ BPheo, $BChl^- \rightarrow$ BPheo) results obtained by Warshel's microscopic method $E_s \approx 0.2 \pm 0.1$ eV (more precisely 0.17, 0.22 and 0.22 eV) [7] practically coincide with the data obtained in our calculations. Hence, in spite of all approximations involved in these two quite different methods of analysis, they give corresponding results, and this agreement provides an important substantiation of the mutual consistency of these two approaches.

TABLE II

Energy parameters of charge transfer reactions, eV

Reagents (donor – acceptor)	E_s	$-\Delta I$	$E^{\ddagger}$
$(BChl)_2^*$ – BChl(I)	0.19	0.2	0.0002
$(BChl)_2^*$ – BChl(II)	0.19	0.0	0.048
$BChl^-$ (I) – BPheo	0.19	0.0	0.048
$BChl^-$ (II) – BPheo	0.19	0.2	0.0002
$(BChl)_2^*$ – BPheo	0.22	0.2	0.0003
(BChl)* – BPheo	0.26	0.2	0.004
$BPheo^-$ – MQ	0.40	0.5	0.002
$BPheo^-$ – Q	0.42	0.5	0.001
MQ^- – $(BChl)_2^+$	0.47	0.65	0.010
$BPheo^-$ – $(BChl)_2^+$	0.22	1.15	1.01
$BPheo^-$ – $(BChl)^+$	0.26	1.15	0.75
$BChl^-$ (I) – $(BChl)_2^+$	0.19	1.15	1.22
$BChl^-$ (II) – $(BChl)_2^+$	0.19	1.35	1.77

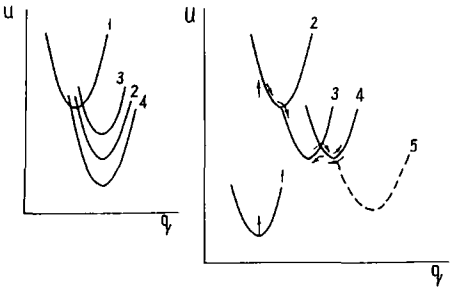

Fig. 1. Scheme of energy terms. Curve 1, initial state; curves 2, 3, 4, final states corresponding to different ΔI values.

Fig. 2. Scheme of energy terms. Curve 1, $(BChl)_2$ in unexcited state; 2, $(BChl)_2^*$; 3, $(BChl)^+$ $BChl^-$; 4, $(BChl)_2^+$ $BPheo^-$; 5, $(BChl_2)^+$ Q^- (all other components, not mentioned in explanations for each curve, are assumed to be each in the ground state).

The second column in Table II gives the ΔI values and the third one the values of $E^{\ddagger}$ calculated by Eqn. 1. For ΔI the rounded figures are given based mainly on the experimental redox potentials for *Rb. sphaeroides* RC summarized in Ref. 24. The energy level for $BChl^-$ was not determined experimentally by direct redox potential measurement. Two different methods of indirect estimates of this level were described in the literature, giving different results. In Table II both variants are given, designated as BChl(I) (according to data of [24]) and BChl(II) [25].

The most important result of these calculations is that for all reactions in the main charge transfer path (special pair → BPheo → Q_A), the activation energy is vanishingly small – its largest value is 4 meV, i.e., 6-times less than kT at room temperature (with the value of $\Delta I = -0.23$ to -0.26 eV for $(BChl)_2^* \rightarrow$ BPheo electron transfer, which seems to be more probable [25,27], the upper limit for $E^{\ddagger}$ decreasis to 1.8 meV). This result accounts for the experimental fact that the charge transfer in RC is activationless.

What are the physical reasons responsible for so small an $E^{\ddagger}$? First, this is the small reorganization energy of proteins (small C_{eff}), which to my mind is one of the most important features of enzymatic catalysis in general [14–16,22]. Second, the reorganization energy is low due to the use of reagents of large effective radius. Third, and this is a very interesting feature of RC, the radii of the reagents are such that the reorganization energy proves to be very well matched to the energy

change in the reaction. Actually, the transition between $(BChl)_2^*$ and BPheo at $\Delta I = -0.2$ eV has the reorganization energy $E_s \simeq 0.2$ eV, and the transition from BPheo to MQ at $\Delta I \simeq -0.5$ eV has $E_s = 0.4$ eV or, taking into account $E_i = 0.04$ eV, $E_r = 0.44$ eV, i.e., again a value very close to that of $-\Delta I$. If nature used as an electron acceptor in place of quinone, for example, some porphyrin with the same redox potential, then ΔI would have the same value, but E_s would be much less – the same as for transfer between two chlorophylls, then the reaction would go into the so-called inverted region and the activation energy would increase to 0.11 eV – a not very high, but still sufficiently significant, value that decreases the reaction rate by two orders. The choice of quinones *, therefore, as acceptors is of biological significance not only from the standpoint of their redox potentials, but also from considerations of the good fit of the geometric parameters of the system with a view of achieving a close correspondence between the reorganization energy and the energy of the reaction.

It should be noted that an exact equality of the quantities E_r and $-\Delta I$ ensuring zero activation energy, or, in other words, the intersection of the initial state term by the final state term precisely at the minimum of the former (Fig. 1, curves 1 and 2), is very unlikely. But an even approximate equality proves to be sufficient in practice, since when the intersection occurs near the term minimum the activation barrier is small both in the normal region (the so-called external intersection of terms, curves 1 and 3) and in the inverted region (internal intersection, curves 1 and 4). The cases of small barriers, when E_r deviates from an exact equality to $-\Delta I$, are to be found in Table II.

It is interesting to mention that, according to Table II, both estimates of the energy level of $BChl^-$ result in some not very high but tangible barrier of about 50 meV: for $BChl^- \rightarrow$ BPheo transfer (variant I) or $(BChl)_2^* \rightarrow$ BChl reaction (variant III). This circumstance, however, cannot be an obstacle for the bridge transfer of electron from $(BChl)_2^*$ to BPheo via BChl.

The similarity of the values of $-\Delta I$ and E_r is responsible for another effect – the very slight influence of the negative charge acquired by Q_A during its reduction on the electron transfer rate from $(BChl)_2$ to BPheo (only 2-fold deceleration [28,29]). The electrostatic interaction of Q_A^- with BPheo and $(BChl)_2$ increases (algebraically) the ΔI of this reaction by 0.13 eV (at $\epsilon_s = 4$). For an ordinary reaction (with $|\Delta I| \ll E_r$), this change of ΔI would result in increase of the activation energy by $\frac{1}{2}\Delta|\Delta I| \simeq 0.06$ eV, which corresponds to 10-fold deceleration. In our case, at $E_s \simeq 0.2$ eV, the value of $E^\ddagger$ is 0.02 eV, which corresponds in practice to a 2-fold decrease of the rate *.

This consideration seems to contradict the experimental data which give much lower effect of quinone reduction on ΔI of electron transfer – only about 0.02 eV [30,31] or 0.03 eV [26]. With these data the maximal deceleration can be evaluated by a too small a value, of 7%. A possible solution of the problem may be based on the fact that the time spans corresponding to the primary charge separation and the back-reaction studied by fluorescence method [26,30,31] are substantially different. During the first process, some modes of nuclear motions (e.g., shift of chromophore positions, large-scale α-helix deformations, etc.) have no time to relax to the equilibrium coordinates. For the back-reaction, however, some relaxation takes place [30]. If we suppose the relaxation to proceed further (or/and faster) in the field of Q^-, then different changes of ΔI for the primary electron transfer to an unrelaxed state and for the back-transfer can be qualitatively understood.

As was pointed out by Jortner [2], for 'picosecond' electron transfer processes one should take into consideration the possibility of an incomplete relaxation of the heavy subsystem, i.e., nuclei. Some experimental evidence is available to date in favour of the existence of relaxation processes such as these (it is summarized in Ref. 24; see also Ref. 30, 32, 33). Though for the pigment molecules themselves we can expect only small changes in the intramolecular coordinates, the changes in the protein surrounding (or/and the pigments intermolecular distances) may be quite significant, i.e., we may expect a significant slow relaxation of the medium. In terms of the energy curves, the picture can be described as follows (Fig. 2). Being excited by light, the system finds itself in the nonequilibrium state. In process of thermal motion it reaches the intersection point of curves 2 and 3 (not necessarily coinciding with the energy minimum of term 2, but according to my calculations for BChl(I), close to it) and passes to term 3. If the thermal relaxation proceeds quickly enough, the system is localized at the minimum 3. A different version is, however, possible. When passing from term 2 to term 3, there is an excess energy, much greater than the energy at the intersection point of terms 3 and 4. If this energy does not dissipate quickly enough, the system manages to go through the intersection point and to pass to term 4, as shown by arrows above the curves of Fig. 2. Having lost its energy, the system becomes localized in the state 4. In the opposite case (the excess energy not expended) it may return to term 3 (the arrow below the curves). Thus, for very fast electron transi-

* Table II also lists the results corresponding to the substitution of MQ by some benzoquinone, Q, of the same redox potential. The difference is, obviously, insignificant.

* A similar conclusion was reached in Refs. 4, 5, where the adjusted value of E_s was used.

tions, for which the relaxation rate of the medium is of essential importance, a transition is possible during one elementary action both into the $BChl^-$ and the $BPheo^-$ state.

Fig. 2 describes our calculations with the first version of the estimate of $BChl^-$ energy level. For the second version, the curve 3 is to be placed higher, a barrier between states 2 and 3 appears which can be surmounted at expense of the excess energy of the nonequilibrium exited state, without any activation via thermal fluctuations. In this version, there is no substantial barrier between states 3 and 4, and the system localizes finally in the lower state 4.

The electron transfer process from $(BChl)_2^*$ to BPheo via BChl is nothing but a bridge electron transfer [34–36]; to be more precise, its special case when its initial state is not one of thermal equilibrium. A question may arise, why, in that case, does the bridge transfer process not go further towards formation of Q^-, since the intersection point of its term 5 with term 4 lies close to the minimum of the latter and thus is lower than the energy of the system at the moment of its transition from term 3 to term 4? In considering this question, one should bear in mind that the real picture of energy terms is much more complicated than is depicted in Fig. 2. Let us illustrate this situation by the example of the mutual arrangement of terms 2, 3 and 4 corresponding to electron localization on $(BChl)_2$, BChl and BPheo, respectively.

As shown above, the transitions $(BChl)_2 \rightarrow BChl$, $BChl \rightarrow BPheo$ and $(BChl)_2 \rightarrow BPheo$ correspond to nearly similar reorganization energies, close to 0.2 eV (for the last-mentioned reaction, E_s is a little larger – by 0.03 – 0.04 eV). The curves of Fig. 2 correspond to the same E_s for the first two reactions, but at great variance with calculation, they give a 4-times larger value of E_s for the transition from term 2 to term 4. The reason for this contradiction lies in the fact that, in principle, a two-dimensional diagram cannot quite adequately describe the multidimensional energy surface. It is impossible to describe the polarization state of the medium by the single coordinate, q, since not only the value but also the orientation of the polarization vector are of importance. The ensuing specific features can be qualitatively explained by means of a three-dimensional diagram (Fig. 3), which shows the system energy as a function of two coordinates of the medium (q_1 and q_2). We see that the values of E_s for the three transitions ($2 \rightarrow 3$, $3 \rightarrow 4$, $2 \rightarrow 4$) are close to one another, which is in complete agreement with calculation. The curve of Fig. 2 describes the energy profile along the reaction path $2 \rightarrow 3 \rightarrow 4$, but it does not apply to the reaction path $2 \rightarrow 4$. The reaction path $2 \rightarrow 3 \rightarrow 4$ actually corresponds to a certain trajectory not in a plane but in space, and this fact leads to important results.

Indeed, let us imagine that the starting point of the

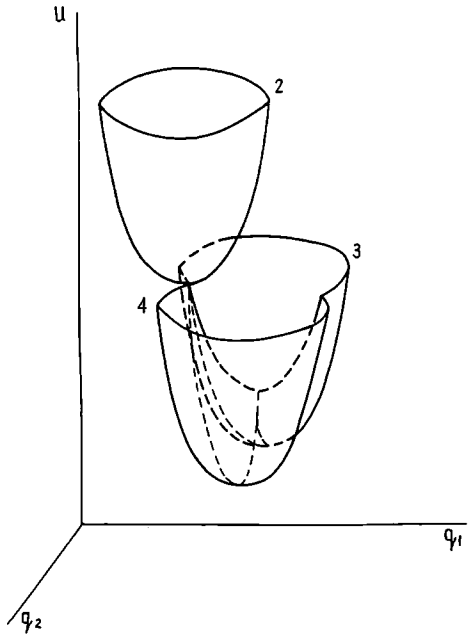

Fig. 3. Three-dimensional scheme of energy terms. Designations as in Fig. 2.

motion of the system on the surface 2 lies exactly in the plane passing through the minima of the parabolloids 2 and 3. In that case the system will pass to term 3 and vibrate in it without passing into the well 4, since it has no momentum in the proper direction. If it acquires this momentum as a result of thermal fluctuations or has it initially, then – and only then – is a transition to term 4 possible. In that case, depending on the arrangement of the terms, a transition not through the saddle point but over it may prove of advantage [36]. The necessity for a distortion of the reaction path decreases the probability of a bridge transition. The transition $2 \rightarrow 3 \rightarrow 4$ includes a single substantial path distortion. A second severe distortion on the path $2 \rightarrow 3 \rightarrow 4 \rightarrow 5$ makes unlikely a bridge electron transition from $(BChl)_2$ directly to Q in one act (the transition $2 \rightarrow 3 \rightarrow 5$ is unlikely due to the large distance between BChl and Q and, hence, a slight overlapping of the electron wave functions). After relaxation in the state $BPheo^-$, further transfer to quinone is practically activationless and can occur at a high rate.

Our calculations allow some other conclusions of a particular nature to be made. As is clear from Table II, the difference in the results for two extreme versions of charge localization in the special pair – equally on both molecules or wholly on one – is not great, so that a more exact determination of the delocalization degree does not introduce any fundamental changes to the results.

The activation energy for the reverse electron transfer from MQ^- to $(BChl)_2^+$ is small (10 meV) and cannot be a serious obstacle to this process. The retardation of the reverse process can, therefore, be explained, in line with the generally accepted concepts, only by the low

probability of electron tunneling for large distances. In that case, the bridge transfer mechanism is ineffective, since the energy levels for particles that could act as bridges lie much higher than the energies of the initial and final state [34–36].

In the last lines of Table II are given the data which show a strong retardation of the reverse electron transfer from $BPheo^-$ (or $BChl^-$) to the special pair to form a neutral $(BChl)_2$ in the ground state. Though this process is thermodynamically advantageous, the reorganization energy is too small compared to $|\Delta I|$, so that the reaction lies far in the inverted region and the activation energy grows drastically. This example clearly shows the significance of the close correspondence of the quantities E_r and ΔI. In principle, this difference between E_r and ΔI can be decreased by formation of $(BChl)_2$ in the vibrationally excited state. But transition to very high vibrational sublevels (necessary to compensate for ΔI) is unlikely. We know of a recombination to form an electronically excited $(BChl)_2^*$, but this reaction is endoergic ($\Delta I \simeq +0.2$ eV) and therefore cannot compete markedly with the reactions in forward direction ($BPheo^- \rightarrow Q$).

The other version is the radical-pair recombination in triplet state. Accepting for the energy difference of $^1(BChl)_2^*$ and $^3(BChl)_2^*$ the value 0.4 to 0.45 eV [27,37] we can calculate for the reaction $^3[(BChl_2)^+ BPheo^-] \rightarrow {}^3(BChl)_2^*$ BPheo the activation energy less than 3 meV. This agrees well with the experimental data on activationless recombination in the triplet state [38]. In spite of its activationless nature, the triplet recombination is much slower than the forward electron transfer due to lower effective preexponential (slow spin rephasing and, possibly, a weaker electronic overlap [38]).

There are not such detailed structural data available for the reaction centres of other photosynthesizing organisms which would permit calculations similar to those presented above. In many respects, however, these centres are similar: the primary acceptor – a compound of the chlorophyll series in energy lies rather near to the primary donor – the photoexcited pigment and then, as a rule, there occurs a more substantial energy drop, the effective radius of the acceptor (quinone or the iron-sulfur cluster) is much less than that of chlorophyll. For this reason we may suppose that in the order of magnitude the estimates given above, which exploit minimal structural information (radii, intermolecular distances), will be useful in discussing other photosynthetic systems.

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