Oscillations in the primary charge separation in bacterial photosynthesis

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This paper examines the temporal evolution of an electron in a photosynthetic reaction center. A model based on self-consistent quantum-mechanical equations is suggested to describe the picosecond transfer of an electron from an excited primary donor, the excited bacteriochlorophyll dimer (P*), to bacteriopheophytin (H). This transfer is shown to have an oscillation behavior. The results obtained offer an explanation for oscillations in the emission kinetics of the primary donor excited state.

1 Introduction

The purpose of this work is to gain a detailed insight into the internal dynamics of the first steps of electron transfer in a photosynthetic reaction center (RC). Ultrafast electron transfer has been studied for a variety of RC complexes where the primary electron donor is an excited bacteriochlorophyll dimer (P*) and the acceptor is bacteriopheophytin (H).[1,2]

After the early measurement of the electron transfer reaction rate, much research has been focused on the role the bacteriochlorophyll monomer (B), which is located between P and H.[3-12]

Two different approaches have been considered. In the first approach, bacteriochlorophyll plays the role of a real intermediate: an electron hops from P* to B and then to H. In the second approach, B serves as a virtual intermediate: an electron jumps from P* directly to H. This case corresponds to super-exchange transfer (Fig. 1). The combination of both approaches is also possible. Despite a large number of theoretical and experimental works devoted to this problem, the temporal evolution of an electron is not completely understood and some details are still unclear.[1,2,13-16]

The application of femtosecond spectrometry has revealed the leading role of vibrational motion in ultrafast processes. This method has enabled the observation of the onset of strongly activated coherent motions and oscillatory features in bacterial reaction centers, indicating coherent motions in the P* state. The detailed characteristics of these motions are essentially unknown.[17-20]

To reveal the relationship between these oscillations and the primary steps of the electron transfer in RC is one of the purposes of this paper. To examine these questions, we consider a simple three-site dynamical model which takes into account both electron and nuclear dynamics.

2 Mathematical model

The electron transfer system of interest here consists of an electron donor (P*) and acceptor (H), connected by a bridge site (B). Our system Hamiltonian has the form:

$$\mathcal{H} = \sum_i \alpha_i |i\rangle\langle i| + \sum_{i,i'} \nu_{i,i'} |i\rangle\langle i'| + \sum_{i,j} \alpha'_{ij} q_{ij} |i\rangle\langle i| \qquad (1)$$

The parameter α_i is the electron energy at site i ($i = 1, 2, 3$ corresponds to P*, B and H respectively), and $\nu_{i,i'}$ are the matrix elements of the electron transfer between sites i and i'. The total site displacements q_{ij} ($j = 1, 2, ..., n_i$) corresponding to n_i frequency modes of the ith site are included; α'_{ij} are the coupling constants of an electron with site displacements q_{ij}.

This Hamiltonian was used to calculate small ionic clusters in describing self-trapped excitons,[21,22] to treat charge transfer in molecular wires,[23,24] and to consider long-range electron transfer in proteins,[25] DNA[26] and other systems.[27]

The equations of motion for Hamiltonian (1) in the neighborhood approximation lead to the system of differential equations (see Appendix):
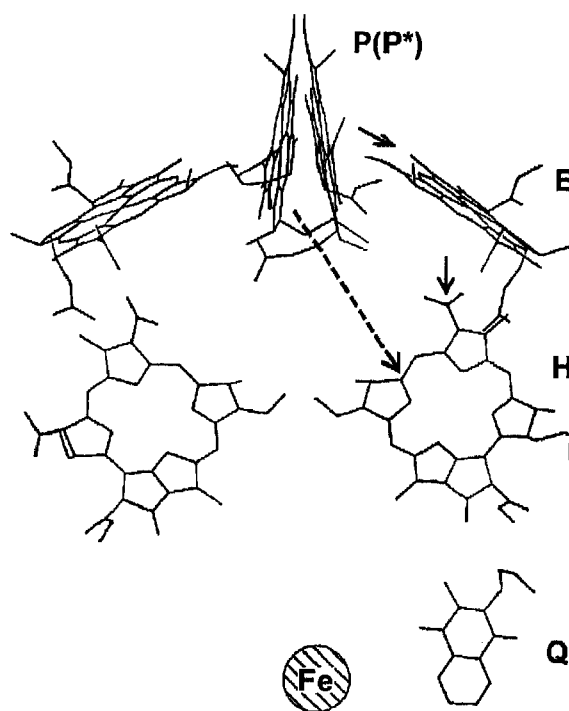

Fig. 1 The photosynthetic reaction center (*Rhodobacter sphaeroides*): full arrows, hopping transfer; broken arrow, superexchange transfer.

$$i\frac{db_i}{d\bar{t}} = \eta_i b_i + \eta_{i,i+1}b_{i+1} + \eta_{i,i-1}b_{i-1} + \sum_j \kappa_{ij}\omega_{ij}^2 u_{ij}b_i \quad (2)$$

$$\frac{d^2 u_{ij}}{d\bar{t}^2} = -\omega'_{ij}\frac{du_{ij}}{d\bar{t}} - \omega_{ij}^2 u_{ij} - |b_i|^2 \quad (3)$$

Here eqn. (2) represents Schrödinger equations for the probability amplitudes b_i describing the excitation evolution in the deformed chain, and eqn. (3) represents the classical equations of motion.

The quantities involved in eqns. (2) and (3) relate to the parameters of Hamiltonian (1) as:

$$\eta_i = \tau\frac{\alpha_i}{\hbar}, \quad \eta_{ii'} = \tau\frac{\nu_{ii'}}{\hbar}, \quad \omega_{ij}^2 = \tau^2\frac{k_{ij}}{M_{ij}},$$

$$\kappa_{ij}\omega_{ij}^2 = \tau^3\frac{(\alpha'_{ij})^2}{M_{ij}\hbar}, \quad q_{ij} = \beta_{ij}u_{ij},$$

$$\beta_{ij} = \tau^2\frac{\alpha'_{ij}}{M_{ij}}, \quad t = \tau\bar{t} \quad (4)$$

where $\hbar$ is the Planck constant divided by 2π; τ is an arbitrary time scale relating the time t and the dimensionless variable $\bar{t}$ in terms of which the differentiation in eqns. (2) and (3) is performed; and M_{ij}, k_{ij} and ω'_{ij} are the mass of the ith site, site elastic constants and damping frequencies corresponding to mode j respectively.

The considered system, eqns. (2) and (3), is self-consistent: the evolution of amplitudes b_i are determined by site displacements u_{ij}, which in turn depend on probabilities $|b_i|^2$.

3 Parameters of electron transfer

The model introduced involves a large set of parameters, which are only partially known.

Energy levels

The ultrafast electron transfer from P* to H indicates that P* and H electron levels are close together. Actually only the difference in the free energy between P* and H can be measured experimentally. The analysis of experimental data leads us to the following estimations for the free energy differences:[19] $\Delta G_1 = -0.041$ eV for the transition from P* to B, and $\Delta G_2 = -0.05$ eV for the transition from B to H. Thus $\Delta G = \Delta G_1 + \Delta G_2 = -0.091$ eV for the transition from P* to H. These values can be used to evaluate the energy levels, $\alpha_i + \sum_j \alpha'_{ij}q_{ij}$ in Hamiltonian (1).

Matrix elements

These values cannot be measured experimentally. Exchange integrals $\nu_{i,i'}$ can be calculated quantum-chemically or can be estimated from the kinetics of the electron transfer. The absolute values of the integrals cannot be calculated with any accuracy.[2] Marcus[16] takes $\nu_{12} = 17$ cm^{-1} and uses the relation $\nu_{23} = 2\nu_{12}$; Jortner et al.[15] put ν_{12} to lie in the interval 17 cm$^{-1} \leq \nu_{12} \leq 100$ cm^{-1} and use the relation $\nu_{23} = 4\nu_{12}$; Holzwarth and Müller's[19] estimation is $\nu_{12} = 19$ cm^{-1} and $\nu_{23} = 20$ cm^{-1}; and in our calculations $\nu_{12} = \nu_{23} = 80$ cm^{-1}.

Frequencies

For the *Rhodobacter sphaeroides* bacteriochlorophyll dimer P, five main frequencies, *i.e.* 15, 92, 122, 153 and 329 cm^{-1}, were obtained.[17,20,28] For the *Rhodobacter sphaeroides* bacteriochlorophyll monomer, the main frequencies were found[14] to be 12 and 30 cm^{-1}. The dominant frequency for H estimated in ref. 2 is equal to 565 cm^{-1}.

Much less is known about the damping of these vibration modes. According to ref. 28, at low temperature, the damping of oscillatory features occurs concomitantly with the decay of the P population in ~1 ps. In our calculations we choose the values of vibration damping less than the values of frequencies, *i.e.* corresponding to the coherence regime of vibration motions.[28]

4 The results of numerical calculations

Numerical integration of eqns. (2) and (3) was carried out by the Runge–Kutta method. At the initial moment the electron was assumed to be localized at P*, $|b_1(0)|^2 = 1$, and the normalization condition $\sum|b_i|^2 = 1$ was used to make sure that the calculations are accurate.

The values of physical parameters considered above lead to the following values of dimensionless parameters of the system of eqns. (2) and (3): $\eta_{11} = 0$, $\eta_{22} = -0.2$, $\eta_{33} = -0.32$, $\omega_{11}^2 = 0.0009$, $\omega_{12}^2 = 0.0339$, $\omega_{13}^2 = 0.0595$, $\omega_{14}^2 = 0.094$, $\omega_{15}^2 = 0.433$, $\omega_{21}^2 = 0.000576$, $\omega_{22}^2 = 0.0036$ and $\omega_{31}^2 = 1.25$. Electron matrix elements are $\eta_{12} = \eta_{23} = 0.15$.

The values of the coupling constants κ_{ij} were chosen in order to get the experimental value of the electron transfer from P* to H and the free energy of electron transfer reaction $\Delta G = -0.091$ eV and are $\kappa_{11} = 0.25$, $\kappa_{12} = 0.05$, $\kappa_{13} = 0.05$, $\kappa_{14} = 0.015$, $\kappa_{15} = 0.32$, $\kappa_{21} = 0.58$, $\kappa_{22} = 0.3$ and $\kappa_{31} = 0.48$.

The damping frequencies were chosen equal to $\omega'_{11} = 0.04$, $\omega'_{12} = 0.02$, $\omega'_{13} = 0.025$, $\omega'_{14} = 0.027$, $\omega'_{15} = 0.5$, $\omega'_{21} = 0.1$, $\omega'_{22} = 0.1$ and $\omega'_{31} = 1.12$.

Fig. 2 shows the oscillation behavior of the time dependence of the probabilities $|b_i|^2$. For a short period the electron oscillates between P* and B and then transfers to H. For the chosen values of the parameters the time of electron transfer is about 1 ps. As is seen from Fig. 2 the electron motion through sites is strongly correlated: the oscillation of electron density on each site has the same oscillation period. The appearance of a non-zero electron density at site B, which exists there for a short period, indicates the creation of a collective excited state (of polaron type[29]).

Fig. 3 shows the time dependence of displacements u_{ij} from their equilibrium positions during the processes of electron transfer. The existence of nonzero displacements on site B is indicative of non-superexchange transfer, *i.e.* B is not a virtual intermediate. At the same time B is not a chemical site on which an electron jumps during the transfer because the displacement u_{2j} does not correspond to their relaxed values.

Fig. 4 shows the comparison of electron energy level modulation on P*, $\Delta E = \sum\alpha'_{1j}q_{1j}$, with the experimental data on the absorption oscillation of *Rhodobacter sphaeroides* bacteriochlorophyll dimer P* due to the coherent vibration motions.[17] It is seen from Fig. 4 that the behaviors of $\Delta E(t)$ and the absorption curve are quantitatively similar.

5 Discussion

The fundamental problem of the description of chemical reactions from the viewpoint of quantum mechanics lies in the irreversible nature of some of these reactions. An approach analogous to ours was developed in ref. 30, but there the interaction with vibration motions was ignored. As a result only reversible evolution of an electron in a photosynthetic system was obtained.

In order to describe the irreversible electron transfer based on the three-site Hamiltonian of type (1), the interaction between vibrations was considered in ref. 31. To model the irreversible transfer a large number of vibrational excited states were taken into account. The results obtained in ref. 31
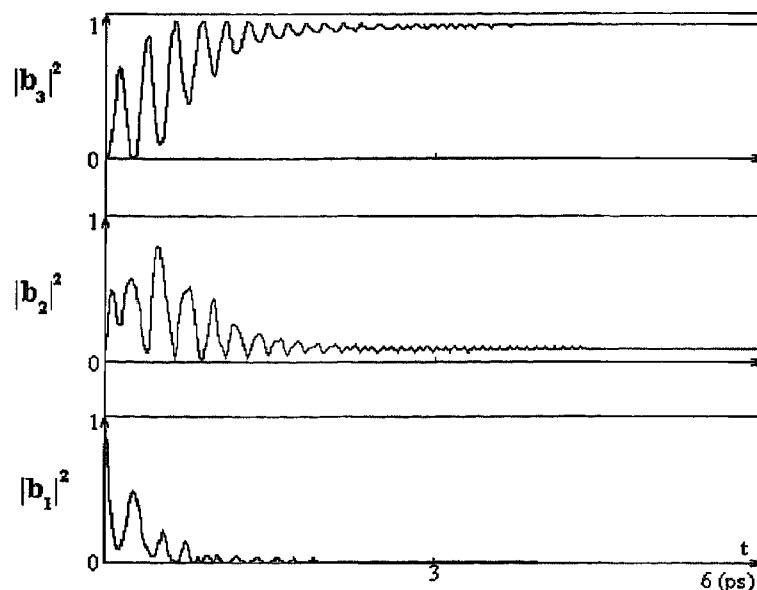
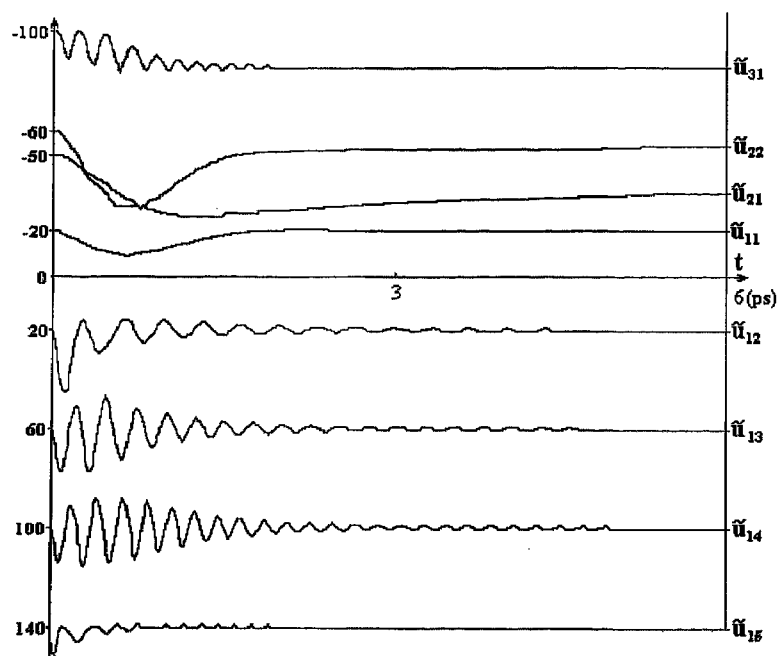**Fig. 2** Time dependence of electron probabilities $|b_i|^2$.

Fig. 3 Time dependence of site displacements u_{ij}: $\tilde{u}_{11} = 0.05u_{11} - 20$, $\tilde{u}_{12} = u_{12} + 20$, $\tilde{u}_{13} = u_{13} + 60$, $\tilde{u}_{14} = u_{14} + 100$, $\tilde{u}_{15} = 5u_{15} + 140$, $\tilde{u}_{21} = 0.1u_{21} - 50$, $\tilde{u}_{22} = 0.3u_{22} - 60$, $\tilde{u}_{31} = 20u_{31} - 100$.

do not reveal the oscillation behavior of the spectroscopic values of the studied system.

Based on the reversible Schrödinger eqn. (2), we have introduced the interaction with vibration modes and demonstrated the irreversible transfer in the considered three-site P*, B, H model having entered friction into the classical equation of motion eqn. (3). As a result of interaction between an electron and vibrations the latter lead to oscillatory features which are very similar to those measured in absorption spectra (Fig. 4).

The results obtained confirm the coexistence of superexchange and sequential mechanisms at the early steps of photosynthesis. Three points following from Figs. 2 and 3 support this conclusion: (1) the oscillations of the electron density between P*, B and H at the initial moments of charge separation; (2) the electron state on site B is not relaxed; (3) the transfer from B to H is not purely irreversible—a small value of electron probability on site B always exists.

6 Concluding remarks

The kinetic analysis of the early steps of photosynthesis is often performed in terms of exponential reactions between individual states. It is shown that $P^* \rightarrow P^+B^-$ and $P^+B^- \rightarrow P^+H^-$ reactions take place on a faster time scale than vibrational relaxation of P^*, B^- and H^- states, indicating that their description in terms of thermally equilibrated states is not valid. This leads to the conclusion of the basic inadequacy of the exponential description. The model considered suggests that the reactions occur near the adiabatic regime and exhibit time oscillations depending on the oscillations of potential energy surfaces of P^*, P^+B^- and P^+H^- states.

The results obtained offer an explanation for oscillations in the emission kinetics of the primary donor excited state. The oscillating picture of an electron delocalized on P, B and H can provide a basis for the theory of photosynthetic reaction.
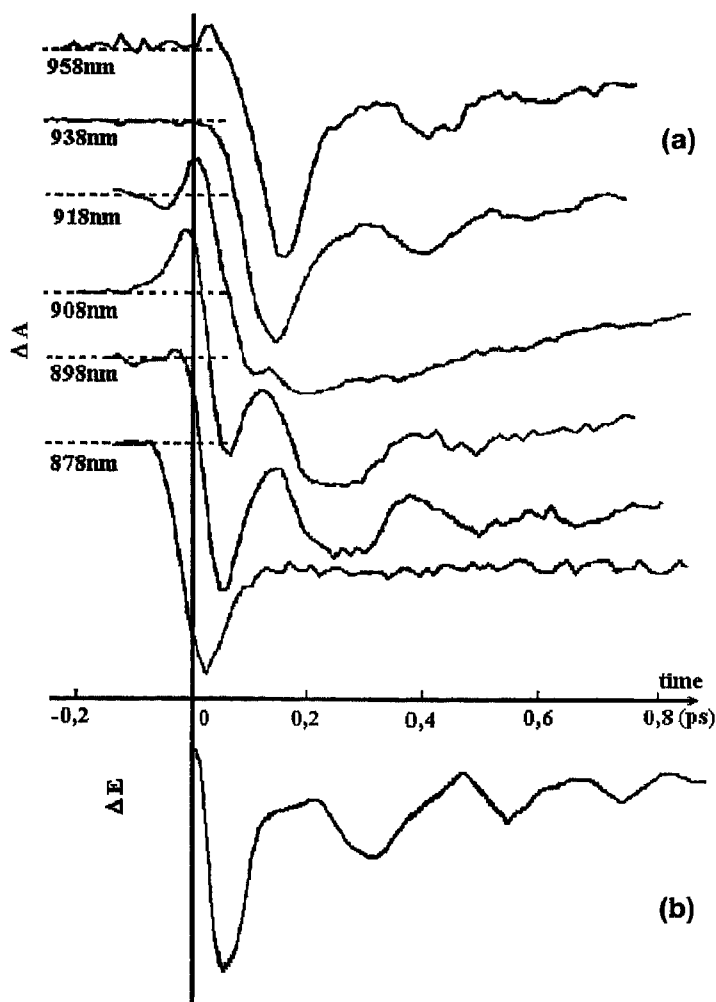
Fig. 4 Comparison of (a) the experimental time dependences of absorption curves $\Delta A(t)$ of an electron with (b) the calculated modulation of electron energy of P^*, $\Delta E(t)$.

Appendix

We will show that the Hamiltonian $\mathscr{H}$ of eqn. (1) leads to the system of differential eqns. (2) and (3). Let us seek the solution of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \mathscr{H}|\Psi\rangle \qquad (A1)$$

in the form $|\Psi\rangle = \sum_n b_n(t)|n\rangle$, where $b_n(t)$ is the probability amplitude describing the excitation evolution on the site n. Substituting $|\Psi\rangle$ in (A1) and taking into account that $\nu_{ij} = \nu^*_{ji}$ we will get for $b_n(t)$

$$i\hbar \frac{\mathrm{d}b_n}{\mathrm{d}t} = \alpha_n b_n + \sum_j \alpha'_{nj} q_{nj} b_n + \sum_{n'} \nu_{nn'} b_{n'} \qquad (A2)$$

With the use of transformations eqns. (4), eqn. (A2) in the neighborhood approximation takes the form of eqn. (2).

The displacements q_{nj} can be described by the classical equation of motion because the site masses are much larger than the electron one. To derive this equation let us introduce the site kinetic energy $T = \sum_{nj} M_{nj} \dot{q}_{nj}^2/2$ and potential energy $U = \sum_{nj} k_{nj} q_{nj}^2/2$ where M_{nj} and k_{nj} are the effective masses and the elastic constants of n_j site oscillator. The total Hamiltonian H averaged over the state $|\Psi\rangle$ takes the form

$$\langle \Psi|H|\Psi\rangle = T + U + \langle\Psi|\mathscr{H}|\Psi\rangle \qquad (A3)$$

The equations of motion for the Hamiltonian (A3) take the form

$$M_{ij} \frac{\mathrm{d}^2 q_{ij}}{\mathrm{d}t^2} = -\gamma_{ij} \dot{q}_{ij} - k_{ij} q_{ij} - \alpha'_{ij} |b_i|^2 \qquad (A4)$$

where γ_{ij} are friction coefficients. With the use of transformations eqns. (4), eqns. (A4) takes the form of eqn. (3).

Acknowledgement

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