MOLECULAR BIOPHYSICS

New Method for Calculating the Dissipation Parameters in Ultrafast Biochemical Reactions from Protein Crystal Structure Data

I. O. Glebov and V. V. Eremin
Chemical Faculty, Moscow State University, Moscow, 119991 Russia
e-mail: glebov_io@mail.ru
Received February 1, 2012; in final form, April 4, 2012

Abstract—A new method of calculating the spectral function of system–bath interaction during an elementary biochemical reaction is proposed. This method was applied to the primary electron transfer in the photosynthetic reaction center of purple bacteria Rhodobacter sphaeroides. The calculated spectral functions differ significantly from the commonly used ohmic function. It is shown that the unidirectionality of the electron transfer along the A-branch in the reaction center of Rh. sphaeroides can be caused by the asymmetry of the reaction system interaction with the protein environment.

Keywords: Redfield theory, electron transfer, photosynthesis, purple bacteria
DOI: 10.1134/S0006350912040069

INTRODUCTION

The specific features of ultrafast biochemical and biophysical processes initiated by light [1–4], such as energy transfer in light–harvesting antennae [5–7] or primary electron transfer in the reaction centers (RCs) of photosynthetic organisms [8–10], are in great measure determined by the protein environs of the reaction system. Protein not only plays a structure-forming role but also indirectly partakes in the reaction. Owing to the interaction of the protein environs with the reaction system the latter undergoes vibrational relaxation, manifesting itself as energy dissipation and loss of coherence of vibrational motion. The protein thereby performs a thermostat function. This phenomenon, on the one hand, leads to a decline in the performance of the photosynthetic device, but on the other, energy dissipation reduces the probability of back transfer, increasing the product yield, and also precludes ‘overheating’ [11] and destruction of the system at excessive absorption of light energy. To add, as we will show here, the protein environs can ensure selectivity if there are competing processes.

Ultrafast reactions in photosynthetic systems proceed under conditions of nonequilibrium vibrational distribution, and their description requires taking into account the quantum effects. A widespread approach in the quantum theory of open systems is the Redfield theory [12]. Initially developed for describing phenomena related to magnetic resonance, at present it is also successfully applied for modeling the biochemical processes [13]. However, application of the mathematical apparatus of this theory to complex molecular objects requires thorough checking and substantiation. Thus for example, the secular approximation, whereby a large number of matrix element is equated to zero in averaging over a certain time interval, is inapplicable to ultrafast processes in the femtosecond range.

Another question, which this paper is devoted to, is the particular form of the dependence of the intensity of system interaction with the thermostat vibrational modes on their frequency, \( J(\omega) \). In most works concerning both model calculations [14–17] and attempts to describe the dynamics of a real process [13, 18–21], use is made of the so-called ohmic function, or ohmic function with exponential trail:

\[
J(\omega) = \eta \omega \exp\left(-\frac{\omega}{\omega_c}\right).
\]  

Such an approach is based on assuming a constant friction coefficient [22], which may be incorrect in the case of complex biological molecules. Besides, the parameters used are phenomenological and are not directly related to the structure of the molecular system.

In this context, a question arises of building, in the framework of the Redfield theory, an adequate model for calculating the parameters of influence of the protein environs on the system where biochemical processes take place. Here we propose a new method of calculating the spectral function from the data on protein structure. Application of this method to the pri-
mary stages of electron transfer in the RC of purple bacteria *Rhodobacter sphaeroides* has allowed explaining the asymmetry of the electron transfer pathway (via the A-branch).

**THEORY**

The Redfield theory proceeds from separating the object into two parts: observable (further, the system) and unobservable (thermostat or bath) [23]. In the RC, the system is a donor–acceptor pair in which electron transfer takes place, while the role of the bath is performed by the protein environs. The complete Hamiltonian subject to such partitioning appears as follows:

\[ H = H_S + H_B + H_{SB}, \]

where \( H_S \) is the system Hamiltonian taking into account the specifics of the reaction: number of electronic states, potential energy surface (section), interaction between electronic states; \( H_B \) is the bath Hamiltonian, regarded as a set of a large number of vibrational modes:

\[ H_B = \sum_k \hbar \omega_k (\hat{a}_k^+ \hat{a}_k + \frac{1}{2}) \]

+ anharmonic summands;

\( H_{SB} \) is the Hamiltonian of system–bath interaction. The general density matrix is factorized in the form:

\[ \rho(t) = \rho_S(t) \rho_B(0), \]

\[ \rho_B(0) = \exp(-\beta H_B)/Z, \]

where \( \rho_S = \text{tr}_B(\rho) \) is the reduced density matrix of the system (RDM, further simply \( \rho \)) obtained by averaging over bath coordinates, \( \rho_B(0) \) is the bath density matrix, which is time-independent and has an equilibrium Boltzmann form, \( \beta = 1/kT \), \( Z \) is the sum over bath states.

The main question unsolved in the Redfield theory framework is the particular form of the interaction Hamiltonian. The simplest version originates from the notion of smallness of the interaction, which allows representing this operator in a form linear with respect to all vibrational coordinates of both bath and system [15]:

\[ H_{SB} = (|1\rangle\langle 1| + |2\rangle\langle 2|) \sum_{kq} g_{kq} (b_k^+ a_q + b_k a_q^+), \]

where \( b_k^+ \), \( b_k \), \( a_q^+ \), \( a_q \) are operators of creation and annihilation for system and bath respectively, \( |1\rangle \) and \( |2\rangle \) are projectors on the electronic states of the reaction system, \( g_{kq} \) are coefficients for the intensity of interaction of the system and bath vibrational modes. These coefficients are described by a spectral function

\[ J_k(\omega) = 2\pi \sum_g g_{kq}^2 \delta(\omega - \omega_q). \]

In the case of a bath with a large number of vibrational modes, as typical of proteins, the spectral function can be regarded as continuous. In the bilinear approximation (5) all the information on system–bath interaction is contained in the spectral function \( J(\omega) \). We propose a new method of describing and calculating this function from the data on the geometric structure of the protein (bath) and its normal modes.

Consider a general electron–nuclear Hamiltonian of the RC:

\[ H = \sum_{n = a, A, i} \frac{p_n^2}{2m_n} + \sum_{n, m = a, A, i} \frac{q_n q_m}{r_{nm}}, \]

where \( p_n \) is the operator of momentum of a particle of mass \( m_n \), \( r_{nm} \) is radius vector, \( q_n \) is charge; summation is made over nuclei (\( a \)) and electrons (\( i \)) of the reaction system, and also over nuclei (\( A \)) and electrons (\( I \)) of the protein. The general Hamiltonian can be presented in the form (2), where \( H_B \) is the protein Hamiltonian, \( H_S \) is the Hamiltonian of the reaction system (donor–acceptor pair), and the rest of the summands constitute \( H_{SB} \):

\[ H_B = \sum_{n = a, A, i} \frac{p_n^2}{2m_n} + \sum_{n, m = a, A, i} \frac{q_n q_m}{r_{nm}}, \]

\[ H_S = \sum_{n = a, i} \frac{p_n^2}{2m_n} + \sum_{n, m = a, i} \frac{q_n q_m}{r_{nm}}, \]

\[ H_{SB} = \sum_{n = a, i} \frac{q_n q_m}{r_{nm}^2} + \sum_{n, m = a, i} \frac{q_n q_m}{r_{nm}^2} + \sum_{a, A} \frac{q_a q_A}{r_{aA}^2}, \]

\[ + \sum_{i, I} \frac{1}{r_{iI}^2} - \frac{q_i}{r_i^2} - \frac{q_A}{r_A^2} \]

\[ = V(r_{ar}, r_a, r_d, r_I) = V(r_{ar}, r_a) + V(r_n, r_d) + V(r_n, r_I) \]

Such partitioning with the help of some reasonable assumptions will allow us to find the coefficients of expansion (5), using the structural and spectral data on the protein environs.

Let us present the protein Hamiltonian as a sum over adiabatic electronic states:

\[ H_B = \sum_i H_B, |i\rangle\langle i|, \]

where \( |i\rangle \) is the eigenfunction of the \( i \)-th electronic state, \( H_B, |i\rangle \) is the operator of vibrational energy in this