

A RESONANCE TREATMENT AND ITS APPLICATION TO ELECTRON
TRANSFER REACTIONS IN A PHOTOSYNTHETIC REACTION CENTRE

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A detailed theoretical description of the “resonance treatment” based on Bloch equations is presented for a dissipative two-state system, in the limit of weak coupling between a microscopic subsystem and its environment, using the framework of the “spin-boson” model. For an Ohmic spectral density function, the dynamics of the transition probability for an overdamped regime is applied in the case of the primary electron transfer reaction in a bacterial photosynthetic reaction center.

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1. Introduction

The quantification of a dissipative subsystem moving in a stable potential is an old problem. The quasi-phenomenological descriptions of the subsystem in isolation [1–3] have been replaced by those in which the subsystem and its environment are regarded as forming a closed system which can be described by a Hamiltonian which contains an explicit dissipation mechanism. In this sense, we will consider the approach of Caldeira and

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Leggett [4] where the phenomenon of dissipation is simply the transfer of energy from a single macroscopic coordinate, characterising the state of the subsystem, to the very complex set of degrees of freedom describing the environment. It is assumed that the energy, once transferred, effectively disappears into environment and is not recovered within any time of physical interest. If one accepts that we can quantify the motion of the macroscopic coordinate (see the “quantum measurement paradox” formulated by Schrödinger as the “Cat Paradox” [5]), then different values of this coordinate will correspond to states of the subsystem in interaction with its environment, macroscopically distinguishable. Thermal effects induced by the environment will disturb the interference between these macroscopically different states.

Important phenomena, such as wave packet dynamics in atoms [6], defect tunnelling in solids [7], electron transfer in chemical and biological reactions [8–10], or the problem of the quantum computers [11], are correlated to the effect of quantum coherence destruction by dissipative influences of the environment. In this paper, we shall consider a microscopic subsystem with two states (mTSS) interacting with each other by a so-called tunnelling term. For mTSS, we will consider the two-dimensional space spanned by the two ground states of the double-well potential needed to represent it. The picture of such a description and its validity conditions can be found in Ref. 12. The presence of the tunnelling term assures the coherence between the two states of mTSS, and consequently, between the two macroscopic states, L and R, of the resulting macroscopic dissipative two-state system (TSS) formed by mTSS and its environment. The quantum coherence destruction is induced by the coupling, which in the quantum theory of relaxation is seen as a “loss mechanism”. One can prove that the problem of mTSS—environment interaction can be cast in the form of the spin-boson Hamiltonian, a very efficient theoretical tool used to describe such an interaction (see Appendix). In terms of the spin-boson Hamiltonian [12,13], the two states of TSS are seen as being a spin 1/2 particle. To describe the two states, let us consider $\{|l\rangle, |r\rangle\}$ the basis of the two-dimensional Hilbert space and the Pauli matrix σ_z (in Schrödinger representation), so that $\sigma_z|l\rangle = |l\rangle$ and $\sigma_z|r\rangle = -|r\rangle$. The energy difference, ε , between the two levels involved in a transition belonging to mTSS and the tunnelling term, $\hbar\Delta$, are components of the Hamiltonian H_s of a two-level subsystem (TLS); $H_s = (\varepsilon/2)\sigma_z - (\hbar\Delta/2)\sigma_x$ describes the dynamics of an isolated mTSS. The environment coordinates and all the coordinates of mTSS, other than the two describing the position in one of the two states, L or R, are seen as an ensemble of harmonic oscillators that create the so-called oscillators’ bath. In σ_z -representation, the standard spin-boson Hamiltonian is written

$$H = \frac{\varepsilon}{2}\sigma_z - \frac{\hbar\Delta}{2}\sigma_x + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{m_j\omega_j^2 x_j^2}{2} \right) + \frac{q_0}{2}\sigma_z \sum_j c_j x_j. \quad (1)$$

The third term is the bath Hamiltonian, H_b , and the fourth is the interaction Hamiltonian, H_{coupl} , written assuming linear-coupling hypothesis. In Eq. (1), p_j is the momentum operator, m_j the effective mass, ω_j the oscillator frequency, x_j the coordinate of the j -th oscillator, q_0 a scaling parameter and c_j the coupling strength. The harmonic oscillators’

bath is fully characterised by the spectral density function

$$J(\omega) = \sum_j c_j^2 \frac{\delta(\omega - \omega_j)}{m_j \omega_j}$$

that gives the density of states of bath weighted by the coupling strength between mTSS and environment [12]. In most studies, e.g., electron transfer reaction (ETR), $J(\omega)$ has an Ohmic term, that is, $J(\omega) = \mu\omega \exp(-\omega/\omega_c)$, where μ is a measurable friction coefficient for the dynamics of macroscopic coordinate and ω_c is a high-frequency cut-off that assures convergence.

In this article, we are interested in the problem of the time evolution of TSS when mTSS is weakly coupled to the environment, assuming that this weak coupling is also transferred to the spin-boson Hamiltonian. The dynamics of TSS will be described in Section 2, the resonance treatment's characteristics for its application to ETR and its utilisation to the primary ETR in a bacterial photosynthetic reaction center will be considered in Section 3.

2. Dynamics of the dissipative two state system

The rate constant of non-adiabatic transitions between L and R in the weak-electronic-coupling limit (small $\hbar\Delta$) – when the environment relaxation time is much shorter than the time of effective transition, so that the initial state is an equilibrium one – can be derived by the Kubo-Toyozava formula [14]; this procedure is also applied to the spin-boson model [15,16].

The limit of weak subsystem-environment coupling allows to treat H_{coupl} as a stochastic function of time. The dynamics can be treated in the framework of the quantum theory of relaxation by the density matrix method. To find the macroscopic coordinate, we note that, taking into account the equilibrium states, a position operator can be defined by $q|l\rangle = -(q_0/2)|l\rangle$ and $q|r\rangle = (q_0/2)|r\rangle$. Consequently, the operator q defined by $q = |l\rangle\langle l|q|l\rangle\langle l| + |r\rangle\langle r|q|r\rangle\langle r|$ becomes $q = -(q_0/2)\sigma_z$. Hence, the macroscopic coordinate is $\langle q(t) \rangle = -(q_0/2)\text{Tr}(\rho_{\text{tot}}(t)\sigma_z) \equiv -(q_0/2)S_z(t)$, where ρ_{tot} represents the total matrix density of the complete system and Tr an average over all coordinates of the system. $S_i(t) \equiv \langle \sigma_i(t) \rangle$ (with $i = x, y, z$) is the average value on ensemble of oscillators' bath and of TLS coordinates.

In TSS, and, alternatively, in spin-boson Hamiltonian terms, the transition's scenario is as follows: until $t = 0$, the environment is in equilibrium and mTSS is found in the initial state or in correspondence in state $|l\rangle$ (where the eigenvalue of σ_z is unity). At $t > 0$, the constraint imposed on mTSS is switched off and it evolves under the action of total Hamiltonian to an equilibrium state. In these circumstances we have to follow the reduced density matrix, ρ , which characterises TLS, more precisely the term $\rho_{ll}(t) = \langle l|\rho(t)|l\rangle$ which gives the probability to find the system in the state $|l\rangle$, or equivalently, mTSS in its initial state. The macroscopic coordinate is correlated with the probability $p(t)$ to find mTSS in its initial state by $\rho_{ll}(t) = [1 + S_z(t)]/2 = p(t)$. In order to cast the problem in

term of a resonance treatment, we write

$$H_s = -\frac{1}{2}\vec{\sigma} \cdot \vec{\mathcal{H}} = -\frac{1}{2}\vec{\sigma} \cdot (\hbar\Delta\vec{i} - \varepsilon\vec{k}), \quad (2)$$

where $\vec{\mathcal{H}}$ is “the magnetic field” and \vec{i} and \vec{k} are unit vector of Ox and Oz axes, respectively. In the basis $\{|l\rangle, |r\rangle\}$, H_s has not a diagonal form and $\vec{\mathcal{H}}$ is not parallel to the spin direction. To apply the formalism of magnetic resonance, where the constant magnetic field is parallel to the spin direction, we shall consider a basis rotation which diagonalises the matrix and simultaneously brings the “constant magnetic field” on Oz' axis. From the calculus of eigenfunctions $\{|1\rangle, |2\rangle\}$ and eigenvalues $\{E_1, E_2\}$ of H_s , we obtain

$$\begin{pmatrix} |1\rangle \\ |2\rangle \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} |l\rangle \\ |r\rangle \end{pmatrix}, \quad U = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}, \quad (3)$$

where:

$$\cos\theta = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{r}{\sqrt{1+r^2}}}, \quad \sin\theta = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{r}{\sqrt{1+r^2}}},$$

$$E_1 = \frac{\hbar\Delta}{2}\sqrt{1+r^2}, \quad E_2 = -\frac{\hbar\Delta}{2}\sqrt{1+r^2} \quad \text{and} \quad r = \frac{\varepsilon}{\hbar\Delta}.$$

A new frame $O'x'y'z'$ will correspond to the new basis and the total Hamiltonian H will be obtained by a *similarity transformation*, $H' = U^{-1}HU$. In the $\sigma_{z'}$ representation of the new basis, the total Hamiltonian H' becomes

$$\begin{aligned} H' &= \frac{\hbar\omega_L}{2}\sigma_{z'} + \frac{q_0}{2}\cos 2\theta \sum_a c_a x_a \sigma_{z'} - \frac{q_0}{2}\sin 2\theta \sum_a c_a x_a \sigma_{x'} + \sum_a \left(\frac{p_a^2}{2m_a} + \frac{m_a}{2}\omega_a^2 x_a^2 \right) \\ &= H_s' + \mathcal{H}_{x'}(t)\sigma_{x'} + \mathcal{H}_{z'}(t)\sigma_{z'} + \sum_a \left(\frac{p_a^2}{2m_a} + \frac{m_a}{2}\omega_a^2 x_a^2 \right), \end{aligned} \quad (4)$$

with: $\cos 2\theta = r/\sqrt{1+r^2}$, $\sin 2\theta = -r/\sqrt{1+r^2}$, $\omega_L = \Delta\sqrt{1+r^2}$, $H_s' = (\hbar\omega_L)\sigma_{z'}$. Now, the problem is similar to that of magnetic resonance for a spin 1/2 particle with the loss mechanisms given by $\mathcal{H}_{x'}(t)$ and $\mathcal{H}_{z'}(t)$. In analogy with the resonance magnetic theory, the modes of frequency ω_L that could be obtained from the spectral components of $\mathcal{H}_{x'}(t)$ could lead to transitions to the upper level of TLS. In case of weak transverse RF, such possible transitions do not give a saturation effect. That means, the oscillators' bath acts only to destroy coherence, and in the Schrödinger picture, Markoff and secular approximations [17], the equation of motion of the reduced matrix density becomes a generalised master equation without a term including such transitions [18]. In such circumstances, in the new frame $O'x'y'z'$, the dynamics could be given by the Bloch equations without transverse RF

field. They consider H_{coupl} through the two relaxation times, τ_1 and τ_2 , the longitudinal and the transversal relaxation time, respectively. Their form is [17]

$$\dot{S}_{x'} = -\omega_L S_{y'} - \frac{S_{x'}}{\tau_2}, \quad \dot{S}_{y'} = \omega_L S_{x'} - \frac{S_{y'}}{\tau_2}, \quad \dot{S}_{z'} = \frac{S_{z'}^{(0)} - S_{z'}}{\tau_1}, \quad (5)$$

where here and in the following the superscript “ (0) ” denotes the value in the equilibrium state. In order to solve Eqs. (5), we shall use (as a technique) the rotation matrix induced by transformation of bases. The grand wave function of the complete system is written [19]

$$|\chi\rangle = |l\rangle\Phi_l + |r\rangle\Phi_r = |1\rangle\Phi_1 + |2\rangle\Phi_2, \quad (6)$$

where Φ 's are functions containing the variables of the environment and of mTSS, others than those describing the two coordinates of TLS. Between the spinors of the two bases, the spinor rotation matrix is written [20]

$$\begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \Phi_l \\ \Phi_r \end{pmatrix}. \quad (7)$$

For example, in the basis $\{|l\rangle, |r\rangle\}$ the spinor $(\Phi_l, \Phi_r)^T$ generates the reduced matrix density

$$\rho = \text{Tr}_{\text{bath}}[|\chi\rangle\langle\chi|] = \begin{pmatrix} \langle\Phi_l|\Phi_l\rangle & \langle\Phi_l|\Phi_r\rangle \\ \langle\Phi_r|\Phi_l\rangle & \langle\Phi_r|\Phi_r\rangle \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 + S_z & S_x - iS_y \\ S_x + iS_y & 1 - S_z \end{pmatrix}, \quad (8)$$

where Tr_{bath} means an average on oscillators' bath ensemble. A similar relation will be found for the basis $\{|1\rangle, |2\rangle\}$ (in obtaining Eq. (8), we used $\rho = (1 + \vec{\sigma} \cdot \vec{S})/2$). Considering Eqs. (6) and (8) for the two bases, we recover the rotation matrix of all vectors that is generated by the spinor rotation matrix [21]

$$\begin{pmatrix} S_{x'} \\ S_{y'} \\ S_{z'} \end{pmatrix} = \begin{pmatrix} \cos 2\theta & 0 & -\sin 2\theta \\ 0 & 1 & 0 \\ \sin 2\theta & 0 & \cos 2\theta \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}. \quad (9)$$

The temporal evolution of the system will be characterised by the functions Φ , so that Eqs. (8) and (9) hold at any moment. Regarding Eqs. (6) and (8), we must remark that such forms hold only if we assume a negligible mTSS-mTSS interaction, that is, the complete system could be represented only by one mTSS in interaction with the medium. This approximation can work for a small density of mTSSs. To solve Eqs. (5), we need the *initial conditions* and the *stationary solution*. At $t = 0$, the system is prepared in a pure state and the reduced matrix density is $\rho(0) = (1 + \sigma_z)/2$ for this case (TLS in the initial state $|l\rangle$), so that with $\rho(0) = (1 + \vec{\sigma} \cdot \vec{S})/2$, one obtains $S_x(0) = S_y(0) = 0$ and $S_z(0) = 1$. In the basis $\{|1\rangle, |2\rangle\}$ with Eq. (9) we obtain

$$S_{x'}(0) = -\sin 2\theta, \quad S_{y'}(0) = 0, \quad S_{z'}(0) = \cos 2\theta. \quad (10)$$

At equilibrium, the reduced matrix density is given by

$$\rho^{(0)} = \begin{pmatrix} W_1 & 0 \\ 0 & W_2 \end{pmatrix} = \frac{1}{Z} \begin{pmatrix} \exp(-\beta E_1) & 0 \\ 0 & \exp(-\beta E_2) \end{pmatrix}, \quad (11)$$

with $Z = 2\cosh(\beta\hbar\omega_L/2)$ [12]. From Eq. (11), at equilibrium, one obtains $S_x^{(0)} = S_y^{(0)} = 0$ and $S_z^{(0)} = W_1 - W_2 = -\tanh(\beta\hbar\omega_L/2)$. For our initial conditions, the solution of Eq. (5) is

$$S_x(t) = -\sin 2\theta \cos \omega_L t \exp(-t/\tau_2), \quad S_y(t) = -\sin 2\theta \sin \omega_L t \exp(-t/\tau_2),$$

$$S_z(t) = (\cos 2\theta - S_z^{(0)}) \exp(-t/\tau_1) + S_z^{(0)}. \quad (12)$$

The inverse of the rotation matrix generates the following solution for the measurable macroscopic coordinate:

$$S_z(t, r, T) = \frac{r}{\sqrt{1+r^2}} \left(\frac{r}{\sqrt{1+r^2}} - S_z^{(0)} \right) \exp\left(-\frac{t}{\tau_1}\right) + S_z^{(0)} \frac{r}{\sqrt{1+r^2}} + \frac{\cos \omega_L t}{1+r^2} \exp\left(-\frac{t}{\tau_1}\right). \quad (13)$$

To find the relaxation times, one can use a straightforward perturbation-theoretical calculation. Leggett et al. [12] find that to a second order in the system-environment coupling, the two times are equal. A more accurate calculus, that takes into consideration the fluctuation of ε , gives [13,22]

$$\frac{1}{\tau_1} = \frac{q_0^2}{2\hbar} J(\omega_L) \coth\left(\frac{\beta\hbar\omega_L}{2}\right) \quad \text{and} \quad \tau_2 \equiv 2\tau_1. \quad (14)$$

For quantitative estimations of the decay rate, one can use “the average survival time” that, in accordance with Ref. 23 can be defined by

$$\tau_m = \int_0^\infty \frac{S_z(t) - S_z(\infty)}{1 - S_z(\infty)} dt. \quad (15)$$

It is equivalent to the “mean first passage time”, and its *inverse* will serve as one estimate for the reaction rate constant. Using Eqs. (13), (14) and (15), we find

$$\tau_m = \frac{(r/\sqrt{1+r^2}) (r/\sqrt{1+r^2} - S_z^{(0)})\tau_1 + \tau_2 / \{(1+r^2)(1 + \omega_L^2 \tau_2^2)\}}{1 - S_z^{(0)} (r/\sqrt{1+r^2})}. \quad (16)$$

3. Discussion

The dynamics found in Eq. (13) is a superposition of two terms: an oscillating one (“coherent component”) similar to that occurring for unbiased case ($\varepsilon = 0$), and a pure exponential relaxation (“incoherent component”) which appears only for biased case ($\varepsilon \neq 0$). The consideration of $S_z(t)$ is particularly important in the context of macroscopic quantum coherence issue, where an observation (non-observation) of oscillatory behaviour would be of fundamental signification to our understanding of quantum mechanics. The form of Eq. (13) shows the typical phenomenon of “quantum beats”, reproducing quantum mechanical interference effects. This expression characterises the dynamics of the subsystem in interaction with environment, in the weak coupling limit. The subsystem relaxation could be *underdamped*, *overdamped*, or *slow-overdamped*, depending on the values of the parameters appearing in Eq. (13).

This resonance treatment was used to characterise ETR in a solution for an overdamped regime of decay [24]. In the case of ETR, the two energy levels of TLS involved in the transition are the electronic ground state energies of the reactant, \mathcal{R} (donor + acceptor + solvent, before electron transfer) and of the product, \mathcal{P} (donor + acceptor + solvent, after electron transfer). These levels are constructed in the self-consistent field of all other electrons and nuclei of the complete system, as experienced by the transferring electron for a given nuclear configuration. The environment fluctuations permanently modify the self-consistent field by changing the nuclear (vibrational) configuration and, consequently, the relative position of the two electronic levels involved in a transfer. In this dynamical picture, the electron transfer is produced by an electronic tunnelling process with maximal probability when these levels have the same height. In the weak coupling limit, the weaker influence of \mathcal{H}_I on the levels of TLS makes the fluctuation less intense. Unlike the treatment of Harris and Stodolski [19], Eqs. (5) take into account the manifestation of this fluctuation. The fluctuation leads to the change of the TLS population by influencing the diagonal terms of the reduced density matrix [18]. A most common energetic representation of ETR is that of the free energy curves, where ε is assimilated as the free energy gap (reaction exothermicity) (see e.g., Refs. 25 and 26). The environmental fluctuations permanently change the value of the free energy of the system, changing the occupied vibronic levels. The electron transfer requires the passage from the lowest vibronic level of \mathcal{R} to the lowest vibronic level of \mathcal{P} . As a supplementary remark, we add that our treatment could work in principle even for a stronger coupling if the factor $\sin 2\theta$ that appears in \mathcal{H}_I is small enough (or r is large enough).

As is known, for slow reaction coordinate, such as solvent polarisation and gross protein motion, where in the majority of cases a strong coupling limit is assumed, an *overdamped relaxation* appears [27]. The method of non-interaction blip approximation (NIBA) [12,28] that tackles the problem of time evolution of a subsystem in interaction with its environment is not accurate enough at non-zero bias, weak coupling (dissipation) and low temperature (see e.g., Ref. 22). Physically, the resonance treatment, as it is conceived, approaches principally the regime where NIBA solutions are not sufficiently reliable. In our approach, the overdamped relaxation could be attained in the case of a *non-adiabatic reaction* (a reaction where the rate is much slower than the solvent relaxation) or at the most weakly adiabatic one. This requires a relatively small value of E_R (nuclear reorganisation energy) and a small τ_L (longitudinal relaxation time of the solvent) [24]. To

discriminate the non-adiabaticity character of a reaction, we use the adiabaticity parameter [28], $g = 4\pi\hbar\Delta^2\tau_L/E_R$. If $g \ll 1$, then a non-adiabatic reaction regime could be assumed. Equation (13) predicts an overdamped regime (*OVR*) if the following inequality holds:

$$OVR \equiv \left| \left(\frac{r}{\sqrt{1+r^2}} - S_z^{(0)} \right) \frac{r}{\sqrt{1+r^2}} \right| (1+r^2) \gg 1. \quad (17)$$

Consequently, if r is *large enough*, i.e., for a given exothermicity, the tunnelling term $\hbar\Delta$ is *small enough*, then an overdamped relaxation regime appears.

Next, we will consider as Ohmic spectral density function a Debye form

$$J(\omega) = \frac{\mu\omega_L}{1 + \omega_L^2\tau_L^2}. \quad (18)$$

The Feynman-Vernon influence functional method [29] predicts for such a spectral density function an overdamped relaxation regime in the case of ETR [24,27,28]. From Eq. (14) and with $\alpha = q_0^2\mu/(2\pi\hbar)$, the relaxation times become

$$\frac{1}{\tau_1} = 2\frac{1}{\tau_2} = \frac{\pi\alpha}{1+r^2} \frac{\omega_L}{1 + \omega_L^2\tau_L^2} \coth \frac{\beta\hbar\omega_L}{2}. \quad (19)$$

This approach holds only if in the limit of zero-temperature $1/\tau_2 \ll \omega_L$, so that it must be applied carefully. The validity condition (VC) of this treatment, when $\tau_2^{-1}(T=0)$ is small compared to ω_L , becomes

$$VC \equiv \frac{\pi\alpha}{2(1+r^2)(1 + \omega_L^2\tau_L^2)} \ll 1.$$

If r is small, the overdamped regime could still appear if the ‘‘cos’’ oscillations in Eq. (13) are strongly damped, that is, $\tau_2^{-1} \gg \omega_L$ (not to be confused with the validity condition). From Eqs. (14) and (19), for $r=0$, this condition can be written

$$\frac{\pi\alpha}{2} \coth \frac{\beta\hbar\omega_L}{2} \gg 1 + \omega_L^2\tau_L^2, \quad (20)$$

imposes *large* T to obtain an overdamped relaxation regime and consequently, special care must be taken when this treatment is applied for the unbiased case. For the considered spectral density, we found in Ref. 24 the dimensionless parameter: $\alpha = \tau_L E_R / (\pi\hbar)$; the relation holds for the considered Debye spectral. The resonance treatment, which holds for weak spin-boson coupling, hence requires a relatively small nuclear reorganisation energy. The magnitude of E_R for an overdamped regime is dependent on the other parameters of the problem ($\hbar\Delta, \varepsilon, \tau_L, T$). For a given T and τ_L , relations in Eq. (19) could require, *but not necessarily*, large E_R for the overdamped regime to be attained. Similar conclusions were obtained by Tang and Lin who noted [9] that a smaller $\Delta\hbar$, a higher temperature and larger E_R ‘‘work against the occurrence of oscillatory electron transfer reactions’’. The theoretical results obtained in Ref. 24 were in a good enough agreement with the experimental results

for solvents with short longitudinal relaxation times (such as water and acetonitrile) and for reaction centers in protein, in the limit of non-adiabatic reactions.

Next, with the new relaxation times from Eq. (14), we will consider an application of our treatment to the primary electron transfer in a mutants photosynthetic reaction center of *Rhodobacter spheroides*, in which tyrosine (M)210 is replaced by tryptophan ((M)Y210W). For the usual experimental values of the parameters characterising the reaction center of photosynthetic bacteria [10,25,30–33], $\tau_L = 0.09 \div 0.2$ ps, $\hbar\Delta = 0.001 \div 0.01$ eV and $E_R = 0.01 \div 0.3$ eV (but with larger limits for all of them and specially the last two). To compare our results to those of Najbar and Tachiya [30], we take $\varepsilon = 0.09$ eV and $T = 80$ K their paper, and $\tau_L = 0.1$ ps and $\hbar\Delta = 0.002$ eV. The confidence parameters are $g = 0.13$ and $VC = 2.4 \cdot 10^{-5}$ so that the treatment could be considered a reliable one. With the considered values, we obtain $\tau_m = 152$ ps for $E_R = 0.084$ eV; they are in good accordance with the experimental data [30]. The value of τ_m is much greater than τ_L so that, as also the value of g predicts, the reaction proceeds in a non-adiabatic or at most a weak adiabatic regime. In addition, the relaxation regime is an overdamped one, as it should be for the considered $J(\omega)$, see Fig. 1.

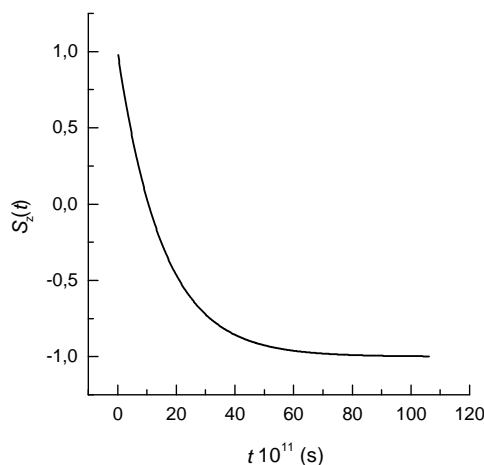


Fig. 1. $S_z(t) = 2p(t) - 1$ for the mutants photosynthetic reaction center of *Rhodobacter spheroides* ((M)Y210W); see the numerical values in text. One obtains an overdamped relaxation and $S_z(\infty) \approx -1$, that is, approximately a unit probability that the reaction will occur.

4. Conclusion

We think the results, obtained here for reaction centers and in [24] for ETR in solutions, could constitute arguments that support the validity of the resonance treatment to describe those ETR that could be considered to be produced in the weak friction limit (or equivalent to this approach, those with good enough confidence parameters). We believe that the

results obtained until now are good reasons to hope that the resonant treatment will result in good results even for weak adiabatic ETR by considering a stronger coupling than that supposed in obtaining Eq. (13). Consequently, consideration of the transverse component of H_{coupl} and a non-Markovian approach could contribute to predict accurately dynamics of dissipative two-state systems by the resonance treatment.

Appendix

Let the states L and R be represented by the Hamiltonians

$$H_L = \sum_j \frac{p_j^2}{2m_j} + U_{Lj}(q_j) + U_{Lj}(0), \quad H_R = \sum_j \frac{p_j^2}{2m_j} + U_{Rj}(q_j) + U_{Rj}(q_j^0), \quad (\text{A.1})$$

where: q_j is the coordinate of the “ j -th” mode in anyone of the two macroscopic states, L or R, $U_{Lj}(q_j)$ and $U_{Rj}(q_j)$ are the potential surfaces of the states L and R, respectively, and $U_{Lj}(0)$ and $U_{Rj}(q_j^0)$ are their minima, and q_j^0 is the distance between the two minima for “ j -th” mode. If we introduce the projection operators $(1 + \sigma_z)/2$ and $(1 - \sigma_z)/2$ on the two possible states (between them the dissipative transition takes place), the Hamiltonian of TSS is written

$$H = -\frac{\hbar\Delta}{2}\sigma_x + \frac{1}{2}(1 + \sigma_z)H_L + \frac{1}{2}(1 - \sigma_z)H_R, \quad (\text{A.2})$$

or

$$H = -\frac{\hbar\Delta}{2}\sigma_x + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{U_{Lj}(q_j) + U_{Lj}(0) + U_{Rj}(q_j) + U_{Rj}(q_j^0)}{2} \right) \cdot \mathbf{1} + \sum_j \left(\frac{U_{Lj}(q_j) + U_{Lj}(0) - U_{Rj}(q_j) - U_{Rj}(q_j^0)}{2} \right) \cdot \sigma_z. \quad (\text{A.3})$$

Comparing Eq. (A.3) with Eq. (1), one can identify

$$q_0 = 1, \quad \varepsilon = \sum_j \frac{U_{Lj}(0) - U_{Rj}(q_j^0)}{2}, \quad c_j x_j = \frac{U_{Lj}(q_j) - U_{Rj}(q_j)}{2}, \quad (\text{A.4})$$

so that, indeed, Eq. (A.2) has a spin-boson Hamiltonian form. For the heat bath represented by harmonic oscillators in the zero-shift approximation between the two states of the “ j ” mode, one can write:

$$U_{Lj}(q_j) = m_j \omega_j^2 q_j^2 / 2, \quad (\text{A.5})$$

$$U_{Rj}(q_j) = m_j \omega_j^2 (q_j - q_j^0)^2 / 2, \quad (\text{A.6})$$

and $c_j = m_j \omega_j^2 q_j^0$, and $x_j = q_j - q_j^0 / 2$ (the correlation between the “ j ” mode of the spin-boson model and the “ j ” mode of TSS).

References

- 1) E. Kanai, Prog. Theor. Phys. **3** (1948) 440;
- 2) M. D. Kostin, J. Chem. Phys. **57** (1972) 3589;
- 3) K. Yasue, Ann. Phys. **114** (1978) 479
- 4) A. O. Caldeira and A. J. Leggett, Ann. Phys. **149** (1983) 374;
- 5) E. Schrödinger, Naturwissenschaften **23** (1935) 807;
- 6) B. M. Garraway and K. A. Suominen, Rep. Prog. Phys. **589** (1995) 365;
- 7) H. Grabert and H. Wipf, *Advances Solid State Physics*, Vieweg Braunschweig (1990), Vol. 30, p.1;
- 8) D. Chandler, *Liquid, Freezing and Glass Transitions*, Les Houches Lectures, ed. D. Levesque et al., Elsevier Science, Amsterdam (1991);
- 9) J. Tang and S. H. Lin, Chem. Phys. Lett. **254** (1996) 6;
- 10) A. Warshel, Z.T. Chu and W.W. Parson, Science **246** (1989) 112;
- 11) A. Garg, Phys. Rev. Lett. **77** (1996) 964;
- 12) A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg and W. Zwerger, Rev. Mod. Phys. **59** (1987) 1;
- 13) U. Weiss, *Quantum Dissipative Systems*, World Scientific, Singapore (1993);
- 14) R. Kubo and Y. Toyozava, Progr. Theor. Phys. **13** (1955) 160;
- 15) C. B. Duke and T. F. Soules, Phys. Lett. A **29** (1969) 117;
- 16) J. Tang, Z. Wang and J. R. Norris, J. Chem. Phys. **99** (1993) 979;
- 17) K. Blum, *Density Matrix Theory and Applications*, Plenum Press, New York (1981), chapt. 7;
- 18) T. Cheche, to be published in Chem. Physics;
- 19) R.A. Harris and L. Stodolsky, Phys. Lett., B **116** (1982) 464;
- 20) E. Merzbacher, *Quantum Mechanics*, John Wiley & Sons, Inc., New York (1970), p. 263;
- 21) L. Landau and E. Lifschitz, *Mecanique Quantique- Theorie non relativiste*, Mir Moscou 1967 p. 242;
- 22) P. Neu and J. Rau, Phys. Rev. E **55** (1997) 2195;
- 23) H. Sumi H. and R. A. Marcus, J. Chem. Phys. **84** (1986) 4894;
- 24) T. Cheche, Chem. Phys. **229** (1998) 193;
- 25) D. Xu and K. Schulten, Chem. Phys. **182** (1994) 91;
- 26) J. Tang, Chem.Phys. **179** (1994) 105;
- 27) J.N. Onuchic, J. Chem. Phys. **86** (1987) 3925;
- 28) A. Garg, J.N. Onuchic and V. Ambegaokar, J. Chem. Phys. **84** (1985) 4491;
- 29) R.P. Feynman and F.L. Vernon, Ann. Phys. (N.Y.) **24** (1963) 118;
- 30) J. Najbar and M. Tachiya, J. Photochem. Photobiol. A: Chem. **95** (1996) 51;
- 31) M. Bixon, J. Jortner and M.E. Michel-Beyerle, Biochim. Biophys. Acta **1056** (1991) 301;
- 32) M. Marchi, J.N. Gehlen, D. Chandler and M. Newton, J. Am. Chem. Soc. **115** (1993) 4178;
- 33) V. Nagarajan, W.W. Parson, D. Davies and C.C. Schenk, Biochimie **32** (1993) 12324.

TEORIJA REZONANCIJA I PRIMJENA NA REAKCIJE ELEKTRONSKOG
PRIJENOSA U FOTOSINTETIČKIM REAKCIJSKIM SREDIŠTIMA

Opisuje se detaljno teorija "rezonantnog postupka" zasnovana na Blochovim jednačinama za disipativan sustav s dva stanja, u granici slabog vezanja mikroskopskog sustava s njegovom okolinom, u okviru "spin-bozon" modela. Uz pretpostavku omske spektralne funkcije gustoće, primjenjuje se dinamika prijelazne vjerojatnosti u natkritično-gušenim uvjetima u slučaju prvotne reakcije elektronskog prijenosa u bakterijskom fotosintetičkom reakcijskom središtu.