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QUANTUM EFFECTS IN BIOMOLECULAR STRUCTURES

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Abstract. Biomolecular structures are potential elements of quantum computers. Results of quantum effects simulation in membrane protein rhodopsin are presented. Important role of the retinal environment and retinal-rhodopsin interactions is revealed. The possibility of rhodopsin use in quantum computation is concluded and dynamics of critical processes is discussed. Simulation is performed in quantum mechanical and molecular dynamics approximation by means of VASP package.

1. INTRODUCTION

Recently, possible quantum nature of processes occurring in biological objects on cellular building block level such as microtubules (MT) and various protein structures was revealed. There is experimental evidence that biomacromolecules (microtubules, DNA chains and other periodical nanostructures) are appropriate object for quantum computation [1].

It was determined that obtaining of the necessary protection from thermal losses and other interactions with environment is possible under specified circumstances. So, macroscopic quantum-mechanical coherence extending over scales that are considerably larger than the atomic scale, may be achieved and saved for times comparable to the characteristic time for biomolecular and cellular processes [2].

One type of quantum systems supposed for use in quantum computation are the ordered high isolated biomolecular structures (DNA, photosynthetic antenna complexes, proteins), which are characterized by long decoherence times. An example of such structure is the membrane protein bacteriorhodopsin containing retinal molecule which existed in two conformations under photoisomerization. It is important to detect the quantum nature of such conformations (states), which are supposed to reveal quantum effects required for quantum computation. Possible spin polarization of electronic states in chromophore is one of these effects.

One of the main goals of this work is to investigate the possibility of the use of biomolecule structure in quantum computation.

Ab-initio simulations were performed by means of VASP code on the supercomputer cluster SKIF [3].

2. STRUCTURE OF PROTEIN RHODOPSIN

The functionality of many proteins is associated with a small subsystem or active site such as a heme group, a couple of amino acids involved in proton transfer, or a co-factor such as an optically active molecule (chromophore). There is a diverse range of optically active molecules that have an important biological function. Examples include retinal (involved in vision), luciferase (green fluorescent protein), and porphyrins (photosynthesis). For these chromophores, the protein acts as a

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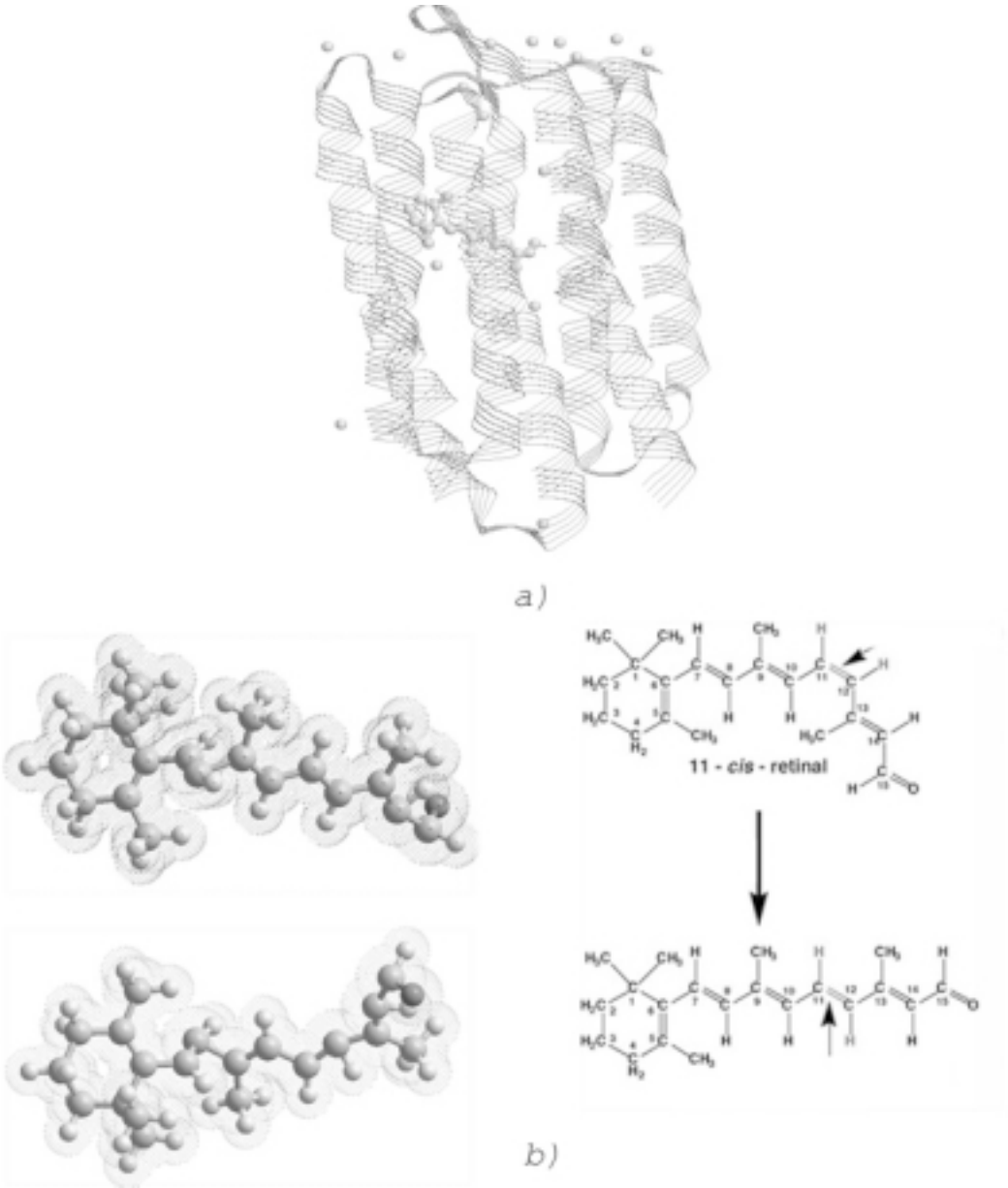

Fig.1. Structure of protein rhodopsin (retinal molecule is located in the center of the protein helixes) (a) and chromophore (retinal) molecule (arrows show place of reconfiguration) (b).

transducer which converts optical excitation of the chromophore into a change in electrical signal or conformational change that, in turn, brings about the desired biological function. Many of these transducers operate with speeds, specificities, and efficiencies which nanotechnologists are striving to mimic [4].

Retinal proteins, often called rhodopsins, are involved in a variety of responses of living cells to light, such as conversion of light to chemical energy and phototaxis in bacteria, or vision in higher organisms. All rhodopsins contain the molecule retinal as their chromophore. Most chromophores are large conjugated organic molecules which are

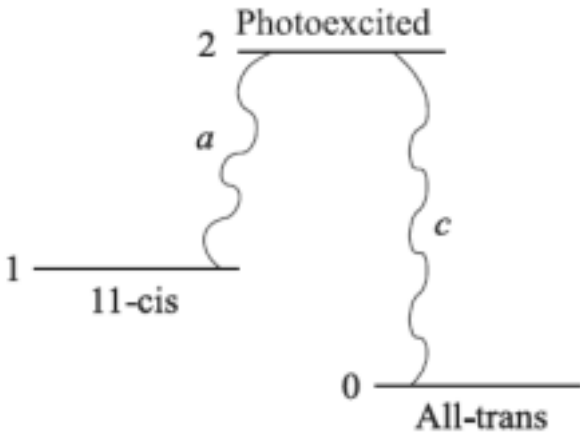

Fig. 2. Model for 3-level states of retinal. Here |0> and |1> are the all-trans and 11-cis states, |2> is the photoexcited state.

surrounded by the protein which in turn is surrounded by a solvent.

The protein rhodopsin, shown in Fig. 1a, consists of seven transmembrane helices. Its chromophore, the 11-cis retinal, is covalently attached to the Lys296 residue of one of the helixes via the formation of a Schiff base.

The activation of rhodopsins is initiated by a photoinduced isomerization of retinal around a specific double bond, which represents one of the fastest chemical reactions in nature [5]. The energy of the absorbed photon is used for the isomerization of the 11-cis retinal isomer to the all-trans one that affects the geometry of the rhodopsin protein.

The initial coordinates of retinal molecule were obtained from the crystal structure of rhodopsin, PDB reference code 1GUE8 (from Protein Data Bank [6]).

3. PROCESSE OF PHOTOEXCITATION OF RHODOPSIN

There were many simulation experiments devoted to process of retinal-rhodopsin photoisomerization [7,8]. And significant role of environment of retinal and chromophor-protein interaction was detected for this process.

A quantum optics model that explains the sensitivity of the dark-adapted rhodopsin to a single photon was presented in recent works [9]. And the absorption of photons by rhodopsin molecules using the three level Λ-type model for its retinal chromophore, with 3 states being the all-trans, 11-cis, and the photoexcited $S1$ state (see Fig. 2). The *ab-initio* calculations have been performed to estimate the parameters of the model. After optical excitation, the retinal chromophore relaxes to the all-trans configuration of the photorhodopsin the first of the intermediates, which is formed in 200 fs after excitation. The process is rather complicated and involves the interaction of the prosthetic group of the retinal with the rhodopsin helices. The energy of the photo-transition to the excited state $S1$ corresponds to the wavelength of 490-570 nm [9]. The formation of the primary all-trans photorhodopsin, that is stable in picoseconds time scale, further decayed in bathorhodopsin, initiates the chain of the photoinduced chemical transformations of rhodopsin.

For this simplified model M. V. Altaisky *et.al* restrict themselves to *ab-initio* quantum chemistry calculations of the retinal ground state energy and dipole momenta in vacuum, for both all-trans and 11-cis configurations [9]. Calculations have been performed with the B3LYP hybrid functional of Becke and the Pople-type 6-31G(*d, p*) basis set as implemented in the *Gaussian'03* software package. The difference in dipole moments (14.56 Debye for 11-cis- and 15.58 Debay for all-trans-retinal) was detected in this work. The results of calculations were short relaxation times and large values of dipole moments. In the process of rhodopsin illumination by one photon per second all emitted photons are transformed into the electron current. Then, the found gain may result in photocurrent about 0.1 μA, that is already a significant macroscopic signal.

The distance between retinals packed in rhodopsin media is of the order of few nm. Since the number of retinal chromophores interacting with the same quantum of light is large, and there may be entanglement effects between the photon field and the quantum ensemble of retinal chromophores, a collective behavior of retinal chromophores is expected. The strength of this collective interaction may depend on many factors: on the energy dissipation within rhodopsin, on the interaction with the solvent, and on the external forces changing the thermodynamic state of the rhodopsin. Estimated coherence length of the collective interaction was $\lambda = 22$ μm [9]. There was suggested that the rod containing rhodopsin can be regarded as a resonator used for the amplification of electronic density waves.

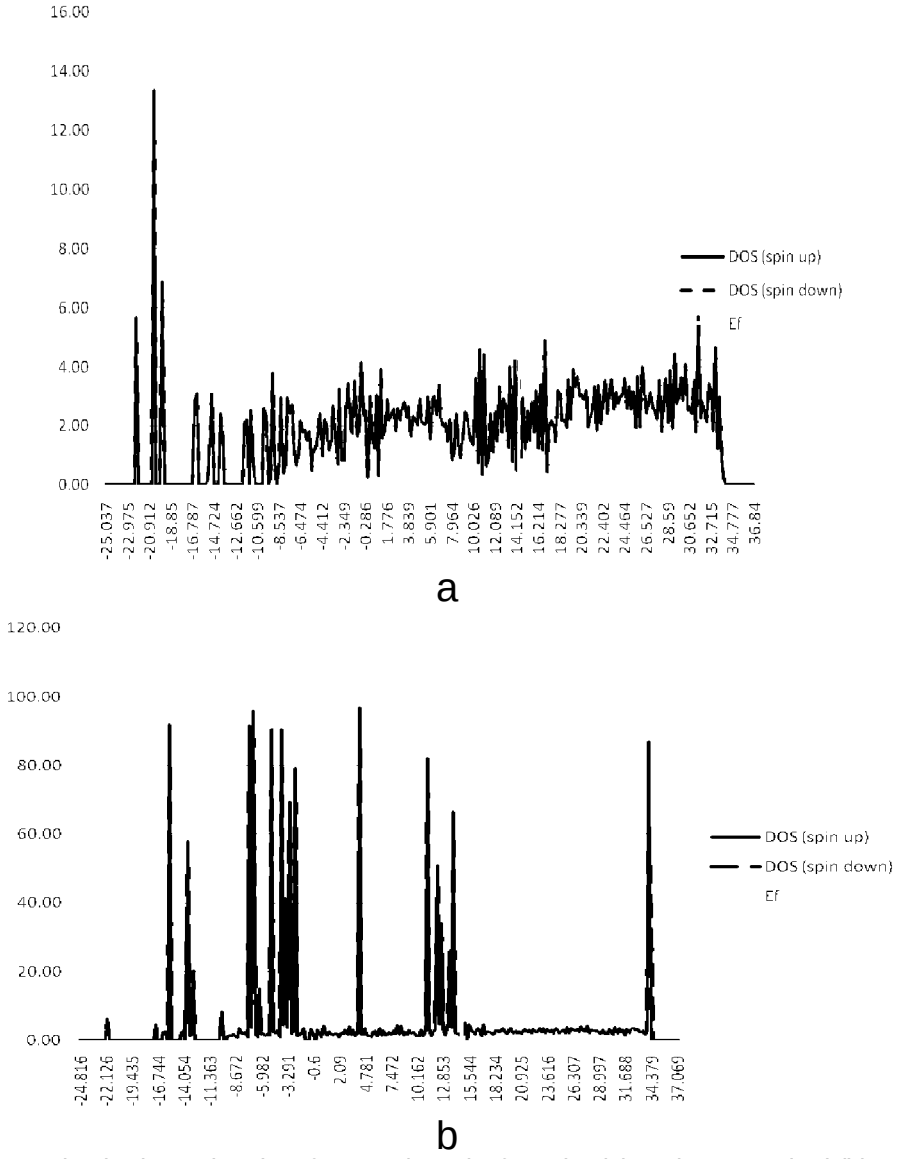

Fig. 3. Spin up and spin down density of states (DOS) of 11-cis- (a) and trans-retinal (b) conformations. Energy values are presented in eV, DOS – in arbitrary units; *Ef* means Fermi energy level.

4. QUANTUM DYNAMICS OF BIOMOLECULAR STRUCTURES

The dynamics of the protein involves thousands of degrees of freedom and at room temperature can be described by classical mechanics and simulated using molecular dynamics methods. In contrast, the functional subsystem involves only a few quantum states and their dynamics must be described with quantum mechanical approach. This has led to considerable effort at developing hybrid QM/MM (quantum mechanical/molecular mechanical) methods.

In most cases the change in quantum state associated with the functional event is associated with a change in the electric dipole moment of the subsystem. Since the protein contains polar molecules and is surrounded by a highly polar solvent (water) there is a strong interaction between the functional subsystem and its environment. Consequently, the environment can have a significant effect on the quantum dynamics of the subsystem.

This interplay between quantum and classical dynamics raises a number of questions of fundamental interest. On what length and time scales does the crossover from quantum to classical behavior occur? When are quantum mechanical effects such as coherence (i.e., superposition states), entanglement, tunneling, or interference necessary for biological function? What aspects and details of the structure and dynamic properties of the protein are crucial to biological function? Indeed, chromophores such as retinal exhibit distinctly different dynamics in solution, in the gas phase, and in the protein environment.

Questions about quantum coherence and the role of the environment are particularly pertinent and controversial in photosynthetic systems.

The quantum dynamics of a quantum system, which is strongly coupled to its environment, is a challenging theoretical problem that has attracted considerable attention over the past few decades. Substantial progress has been made by considering the simplest possible models such as the spin boson model which describes a two-level system (the "spin") which is coupled linearly to an infinite "bath" of harmonic oscillators a_α, a_α^+:

$$H = \frac{1}{2} \in \sigma_2 + \Delta\sigma_x + \sum_a \hbar\omega_a a_a^{\ddot{O}} a_a$$
$$+\sigma_z \sum_a C_a \left(a_a^{\ddot{O}} + a_a\right),$$

where σ_x and σ_z are Pauli spin matrices.

For the spin-boson model, the quantum dynamics is completely determined by a single function, the spectral density, which is defined by

$$J(\omega) = \frac{4\pi}{\hbar} \sum_a C_a^2 \delta(\omega - \omega_a).$$

It describes how strongly the oscillators with frequency near ω are coupled to the two-level system. Many systems are described by ohmic dissipation, for which $J(\omega) = \hbar a\omega$ below some cutoff frequency, ω_c, related to the relaxation rate of the environment, and above which the coupling to the bath of oscillators can be neglected.

Knowledge of the spectral density $J(\omega)$ allows one to make definite statements about whether the quantum dynamics is coherent. For biomolecular systems, the spin-boson model has previously been applied to electron transfer and proton transfer.

An interesting case is when two molecules are coupled by Resonance Energy Transfer (RET), such as rings of chlorophyll molecules in photosynthesis and in Fluorescent Resonance Energy Transfer spectroscopy (FRET). Here, an excitation in one chromophore may be transferred to a nearby chromophore by the Coulomb interaction, typically dipole-dipole interactions. A coupled system of molecules such as this may be mapped to the spin-boson model, where the two quantum states refer to the location of the excitation, $J(\omega)$ describes the coupling of the excitation to the environments surrounding each molecule.

It was shown in [4] that the appropriate spectral density is simply the sum of the spectral density of each individual chromophore-protein complex. The magnitude of the spectral density then determines whether the transfer is coherent (oscillatory) or incoherent (one-way). There are several definite experimental signatures of the coherent interaction of a pair of chromophores. These include splitting of energy levels, super-, and sub-radiance (i.e., increase and reduction of the radiative life time) and changes in fluorescence anisotropy. Both coherence (within a ring) and incoherence (between rings) may play potentially important functional roles in light harvesting complexes.

This approach can be readily adapted to other transitions involving two quantum states which differ in the value of their electric dipole moment. Examples include intersystem crossing, electron, and proton transfer [4].

5. ELECTRONIC STATES OF RETINAL-RHODOPSIN SYSTEM

One of the implementations of quantum nature in retinal may be spin states. Existence of spin polarized electronic states is supposed during the photoisomerization and may be registered by comparing of density of states (DOS) of the 11-cis and the trans-retinal conformations. Spin up and spin down DOS's computed by means of quantum mechanical simulation are presented in Fig. 3. That methodology was used in previous works [10,11]. The calculations have been performed using the *ab-initio* total-energy and molecular dynamics program VASP (Vienna *ab-initio* simulation program) developed at the Institut fur Materialphysik of the Universitat Wien [12-14]. VASP is a complex package for performing *ab-initio* quantum-mechanical molecular dynamics simulations using pseudopotentials or the projector-augmented wave method and a plane wave basis set. The approach implemented in VASP is based on the local-density approximation with the free energy as variational quantity and an exact evaluation of the in-

stantaneous electronic ground state at each MD time step. VASP uses efficient matrix digitalization schemes and an efficient Pulay/Broyden charge density mixing.

Simulations were performed with use of conjugate gradient optimization algorithm and residual minimization scheme, direct inversion in the iterative subspace (RMM-DIIS).

It was supposed that long living time spin polirized electronic states may be generated on photoisomerization process. Such states can play role of quantum bit (qubit) due to their quantum nature. But in only narrow energy gap differences between spin up and spin down DOS are detected in only all-trans-conformation of retinal.

Changes of DOS of all-trans-conformation (larger magnitude of DOS) after photoisomerization mean generation of new electronic states. It conforms good to dipole gain detected in recent works [9].

4. RESULTS AND DISCUSSION

The absence of spin polarized electronic states after photoisomerization does not allow supposed existence of states with quantum behavior. But the rise detected in exited retinal DOS allows the retinal use as photon detector. This change of electronic states may be detected by various methods experimentally. High-speed reaction of photoisomerization means high speed of generation and destruction of electronic states. So, one can detect photon with short time and high efficiency. For example, visual membranes of octopus, whose main component is the light-sensitive signal transducer octopus rhodopsin (octR), are extremely highly ordered, easily capture single photons, and are sensitive to light polarization, which shows their high potential for use as a quantum computer detector [15].

The photoisomerization of retinal is extremely fast, highly selective inside the protein matrix, and characterized through optimal sensitivity to incoming light.

6. CONCLUSIONS

The hybrid QM/MM methods are required for simulation of biomolecular structures due to the quantum behavior of functional subsystem of such structures and important role of this subsystem interactions with environment (for example retinal interactions with rhodopsin). These interactions can have a strong effect on the quantum dynamics of the subsystem.

Absence of spin polarization as one of the possible quantum effects in chromophore-rhodopsin structure was detected. Classical nature of this structure does not allow its use as quantum bit (qubit) in quantum computation. But there is the possibility of its use as photon detector due to the high light sensitivity and new electronic states generation on the photoisomerization detected on DOS in photoexited chromophor.

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