METASTABLE PROCESSES IN PROTEINS

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We have transformed the Scott's model of protein Hamiltonian to metastable form, by means of double coherent unitary transformation. It turned out that in metastable Hamiltonian the number of quasi particles is not conserved due to the forming of pairs of excitations. The energies of pairs are found and their population is quoted. It is interesting that elementary excitations of metastable state behave similarly as excitations of molecular vibration field as well as excitations of electromagnetic field.

1. Specificities of protein structures

Adenosine triphosphate (ATP) molecule is specific represent of proteins. Geometrically it is helicoidal formed of three macromolecules. Proteins are biologically active structures and a good number of biophysical, biological models is based on protein properties. To date a lot of investigations related to proteins were done in soliton theories [1,2]. In a sense of biological role a lot of efforts were devoted to so-called "antisymmetric solitons", but we have shown that antisymmetric solitons are parasitic mathematical solution without physical basis, since they are not cyclically invariant. As a matter of fact, the cyclic invariance is basic property of alpha helicoidal structures, i.e. proteins. The successful model of proteins helicoids was given by Scott [3], where he substituted alpha spiral by the system of interacting discs containing three adenosine molecules located in vertices of equilateral triangle, cf. Fig.1.

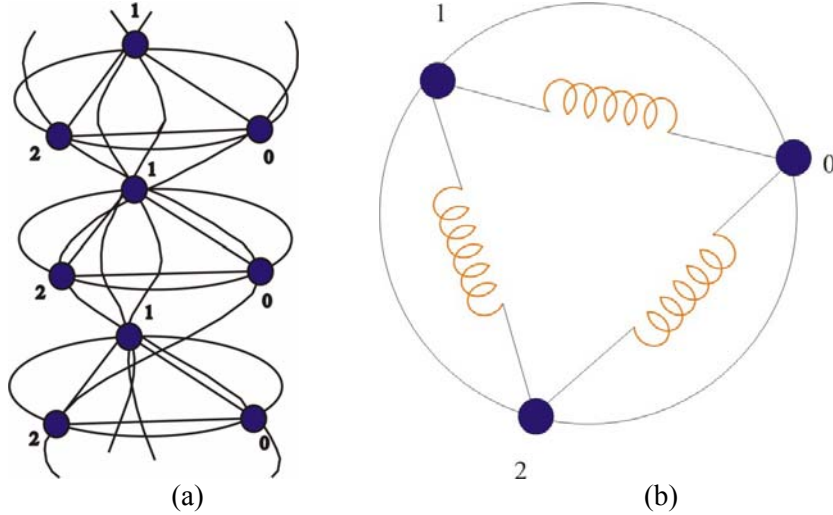[*] Corresponding author: bora@df.uns.ac.rs

Fig.1: (a) Alpha helicoidal structure, and (b) Scott disc with three adenosine molecules

The main property of the system of molecules in disc is cyclic invariance of its physical characteristics which can be expressed as follows:

$$F_n = F_{n+3}$$ (1.1)

Taking into account significance of disc condition, in the first part of analysis we shall investigate some important properties arising from the cyclic invariance. All analyses will be related to one disc.

2. Cyclic invariance of disc

According to Davydov [2] elementary excitations of adenosine molecules are vibrons, i.e. collective waves which appear after exciting internal vibration state of the molecule. This exciting can be achieved by infrared waves whose energies are of the order 1000 k_B. It means that vibrons can be treated as Frenkel's excitons, but without the problems connected with kinematics of operators. As vibration excitations, vibrons are created and annihilated by Bose operators, i.e. they belong to boson field.

Due to cyclic condition from Eq.1.1, for Bose operators B^+ creating excitation in adenosine molecules, it holds:

$$B_n^+ = B_{n+3}^+$$ (2.1)

The Kronecker's symbol in disc can be expressed as follows:

$$\delta_{\nu,\mu} = \frac{1}{3}\sum_{n=0}^{2} e^{i\frac{2\pi}{3}(\nu-\mu)} = \frac{1}{3} e^{i\frac{2\pi}{3}(n+3)(\nu-\mu)}$$ (2.2)

This representation of Kronecker's symbol enables us to use plane waves in transformations of the physical characteristics of disc.

Now we shall examine energies of the vibron excitations in the disc. As it was said above, the vibron Hamiltonian of the disc is of the exciton type and can be written, in the nearest neighbors approximation, as follows:

$$H = \Delta\sum_{n=0}^{2} B_n^+ B_n - \frac{1}{2}W\sum_{n=0}^{2} B_n^+\left(B_{n+1} + B_{n-1}\right)$$ (2.3)

We shall look for energies of vibrons in disc in two manners.
First, we shall look for energies of elementary excitations by means of equations of motion:

$$i\hbar\dot{B}_n = EB_n = [B_n, H] = \Delta B_n - \frac{1}{2}W\left(B_{n+1} + B_{n-1}\right)$$ (2.4)

Taking n = 0, 1, 2 into Eq.2.4, we obtain the system of difference equations from which we obtain the energies:

$$E_1 = \Delta - W \ ; \qquad E_{2,3} = \Delta + \frac{1}{2}W \ . \tag{2.5}$$

As we see, the spectrum of energies in the disc is double degenerated.

Second, in the Hamiltonian (Eq.2.3) we shall take Fourier transformation of operators, and this due to Eq.2.2 becomes:

$$H = \sum_{v=0}^{2} \left(\Delta - W \cos \frac{2\pi}{3}v \right) B_v^+ B_v \ . \tag{2.6}$$

Writing this expression in the expanded form, we have:

$$H = (\Delta - W)B_0^+ B_0 + \left(\Delta - W \cos \frac{2\pi}{3} \right)B_1^+ B_1 + \left(\Delta - W \cos \frac{4\pi}{3} \right)B_2^+ B_2 =$$

$$= (\Delta - W)B_0^+ B_0 + \left(\Delta + \frac{1}{2}W \right)B_1^+ B_1 + \left(\Delta - \frac{1}{2}W \right)B_2^+ B_2 \ . \tag{2.7}$$

As we see from Eq.2.7, the diagonalization of the Hamiltonian has given the same energies as method of equations of motion, and it justifies the abovementioned statement that operators of the cyclic invariant system may be expanded over plane waves.

3. Double coherence unitary transformation of the disc Hamiltonian

The Hamiltonian (Eq.2.3) of the disc in Scott's model of alpha helicoids is relatively simple and obviously cannot reproduce complicated set of processes which occur in proteins. This was the reason for us to provoke the above described existing situation, by looking for some possible metastable states passed by the protein in its way to the stable ground state. The choice was inspired by the fact [4–7] that if external perturbation excites two or more molecules, this causes effect of non-conserving number of elementary excitations. More concretely, exciting more than one molecule give chances for forming the pairs of elementary excitations. Consequently, in this section the subject of analyses will be estimation of possibility of pairing vibron elementary excitations in proteins. This will be done by means of double coherent unitary transformation of Hamiltonian (expressed by Eq.2.3) of the disc. Since this transformation is connected with important effect of quasi-particle non-conservation, we shall generalize derivation of the equivalent Hamiltonian for the cyclic invariant system with N+1 particles.

If we introduce antihermitian operator

$$\hat{S} = \varphi \sum_{n=0}^{N} \left(B_m B_n - B_m^+ B_n^+ \right) \ , \tag{3.1}$$

where B are Bose operators and φ is real parameter, then the unitary transformation of the Hamiltonian:

$$H = \Delta \sum_{n=0}^{N} B_n^+ B_n - \frac{1}{2}W \sum_{n=0}^{N} B_n^+ \left(B_{n+1} + B_{n-1} \right) \tag{3.2}$$

is given by Weyl's identity [8]:

$$H_{eq} = e^{-\hat{s}} H e^{\hat{s}} = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \underbrace{[S, [S, [S, ... [S, H]]]]}_{k-\text{times}} \ . \tag{3.3}$$

It turned out that even terms in Eq.3.3 are either constant or proportional to $B^+ B$, while odd terms are proportional to $BB + B^+ B^+$. So we obtain the equivalent Hamiltonian in the form:

$$H_{eq} = E_0 + H_d + H_{nd} \ , \tag{3.4}$$

where

$$E_0 = \frac{1}{2}(N+1)\Delta(\cosh \varepsilon - 1) \ , \tag{3.5}$$

$$H_d = \sum_{n=0}^{N} \left[\Delta B_n^+ B_n - \frac{1}{2} W B_n^+ \left(B_{n+1} + B_{n-1} \right) \right] \cosh \varepsilon \tag{3.6}$$

$$H_{nd} = -\frac{1}{2} \sum_{n=0}^{N} \left\{ \Delta \left(B_n^+ B_n^+ + B_n B_n \right) - \frac{W}{2} \left[B_n^+ \left(B_{n+1}^+ + B_{n-1}^+ \right) + B_n \left(B_{n+1} + B_{n-1} \right) \right] \right\} \sinh \varepsilon \tag{3.7}$$

In the last formula the notation $4\varphi = \varepsilon$ was used.

As it is seen, the equivalent Hamiltonian has positive ground state energy E_0 with respect to zero ground state energy of the Hamiltonian H. It means that the state with Hamiltonian H_{eq} is not the most stable state, i.e. equivalent Hamiltonian corresponds to metastable state which becomes maximally stable when $\varepsilon \to 0$ (when $H_{eq} \to H$).

The metastable states with Hamiltonian H_{eq} will be examined by means of Green's function method. We shall start from commutator Green's function G (8) and creation pairs Green's function D:

$$G_{nm}(t) \equiv \ll B_n(t) \big| B_m^+(0) \gg = \theta(t) < \left[B_n(t), B_m^+(0) \right] >$$

$$D_{n,m}(t) = \ll B_n^+(t) \big| B_m^+(0) \gg \tag{3.8}$$

After differentiating Eqs.3.8 with respect to time, and the use of equations of motion for operator B_n, we obtain the following equation for G and D:

$$i\hbar \frac{d}{dt} G_{n,m}(t) = i\hbar \delta(t)\delta_{n,m} + \Delta \cosh \varepsilon G_{n,m}(t) - \frac{1}{2} W \cosh \varepsilon \left[G_{n+1,m}(t) + G_{n-1,m}(t) \right] -$$

$$- \Delta \sinh \varepsilon D_{n,m}(t) + \frac{1}{2} W \sinh \varepsilon \left[D_{n+1,m}(t) + D_{n-1,m}(t) \right] \tag{3.9}$$

$$i\hbar \frac{d}{dt} D_{n,m}(t) = -\Delta \cosh \varepsilon D_{n,m}(t) + \frac{1}{2} W \cosh \varepsilon \left[D_{n+1,m}(t) + D_{n-1,m}(t) \right] +$$

$$+ \Delta \sinh \varepsilon G_{n,m}(t) - \frac{1}{2} W \sinh \varepsilon \left[G_{n+1,m}(t) + G_{n-1,m}(t) \right] \tag{3.10}$$

After Fourier time-frequency transformations of (3.9) and (3.10) those equations become:

$$(E - \Delta \cosh \varepsilon) G_{n,m}(\omega) = \frac{i\hbar}{2\pi} \delta_{n,m} - \frac{1}{2} W \cosh \varepsilon \left[G_{n+1,m}(\omega) + G_{n-1,m}(\omega) \right]$$

$$\Delta \sinh \varepsilon D_{n,m}(\omega) + \frac{1}{2} W \sinh \varepsilon \left[D_{n+1,m}(\omega) + D_{n-1,m}(\omega) \right] \tag{3.11}$$

$$(E + \Delta \cosh \varepsilon) D_{n,m}(\omega) = \frac{1}{2} W \cosh \varepsilon \left[D_{n+1,m}(\omega) + D_{n-1,m}(\omega) \right] +$$

$$+ \Delta \sinh \varepsilon G_{n,m}(\omega) - \frac{1}{2} W \sinh \varepsilon \left[G_{n+1,m}(\omega) + G_{n-1,m}(\omega) \right] \tag{3.12}$$

By means of Fourier transformations:

$$G_{n,m}(\omega) = \frac{1}{N+1} \sum_{\nu=0}^{N} G_\nu(\omega) e^{i\frac{2\pi}{3}\nu(n-m)}, \quad D_{n,m}(\omega) = \frac{1}{N+1} \sum_{\nu=0}^{N} e^{i\frac{2\pi}{3}\nu(n-m)},$$

$$\delta_{n,m} = \frac{1}{N+1} \sum_{\nu=0}^{N} e^{i\frac{2\pi\nu}{N+1}(n-m)}, \quad B_n^+ B_m^+ \to \frac{1}{N+1} \sum_{\nu=0}^{N} B_\nu^+ B_{-\nu}^+ e^{i\frac{2\pi\nu}{N+1}(n-m)}, \tag{3.13}$$

the system of equations Eq.3.11 and Eq.3.12 becomes

$$\left[E - \left(\Delta - W \cos \frac{2\pi\nu}{N+1} \right) \cosh \varepsilon \right] G_\nu(\omega) + \left(\Delta - W \cos \frac{2\pi\nu}{N+1} \right) \sinh \varepsilon D_\nu(\omega) = \frac{i\hbar}{2\pi}, \tag{3.14}$$

$$-\left(\Delta - W\cos\frac{2\pi v}{N+1}\right)\sinh\varepsilon\, G_v(\omega)+\left[E+\left(\Delta - W\cos\frac{2\pi v}{N+1}\right)\cosh\varepsilon\right]D_v(\omega)=0,$$

(3.15)

wherefrom is follows:

$$G_v(\omega)=\frac{i\hbar}{2\pi}\frac{E+E_v\cosh\varepsilon}{(E-E_v)(E+E_v)}=\frac{i}{2\pi}\left(\frac{\cosh^2\dfrac{\varepsilon}{2}}{\omega-\omega_v}-\frac{\sinh^2\dfrac{\varepsilon}{2}}{\omega+\omega_v}\right),$$

(3.16)

$$D_v(\omega)=\frac{i\hbar}{2\pi}\frac{E_v\sinh\dfrac{\varepsilon}{2}}{(E-E_v)(E+E_v)}=\frac{i}{2\pi}\sinh\frac{\varepsilon}{2}\cosh\frac{\varepsilon}{2}\left(\frac{1}{\omega-\omega_v}-\frac{1}{\omega+\omega_v}\right).$$

(3.17)

Energy of the system is given by:

$$E_v=\Delta-W\cos\frac{2\pi v}{N+1};\qquad \omega_v=\frac{E_v}{\hbar}.$$

(3.18)

It is seen from Eq.3.18 that energies E_v of the elementary excitations in the metastable state of the Hamiltonian H_{eq} are equal to the energies of the stable state of the Hamiltonian H. This is expectable, since unitary transformations do not change eigenvalues. On the other hand populations of elementary excitations differ in metastable and stable states.

Finding of population requires finding of the Green's function spectral intensity. Spectral intensities of Green's function G and D are respectively (8):

$$J(G)=\underset{\delta\to+0}{=}\frac{G_v(\omega+i\delta)-G_v(\omega-i\delta)}{e^{\frac{E_v}{k_B T}}-1}=\frac{\cosh^2\dfrac{\varepsilon}{2}}{e^{-\frac{E_v}{k_B T}}-1}\delta(\omega+\omega_v),$$

(3.19)

$$J(D)\underset{\delta\to+0}{=}\frac{D_v(\omega+i\delta)-D_v(\omega-i\delta)}{e^{\frac{E_v}{k_B T}}-1}=\sinh\frac{\varepsilon}{2}\cosh\frac{\varepsilon}{2}\frac{1}{e^{-\frac{E_v}{k_B T}}-1}\delta(\omega-\omega_v).$$

(3.20)

Correlation functions are given by:

$$<B_n^+ B_n>=\frac{1}{e^{\frac{E_v}{k_B T}}-1}+\sinh^2\frac{\varepsilon}{2}\coth\frac{E_v}{2k_B T},$$

(3.21)

$$<B_n^+ B_n^+>=\sinh\frac{\varepsilon}{2}\cosh\frac{\varepsilon}{2}\frac{E_v}{2k_B T}$$

(3.22)

and they provide populations of the elementary excitations and of the pairs of elementary excitations.

Ending this part it should be pointed out that for $\varepsilon\to 0$ the metastable system goes over into the stable system. In this case population expressed by Eq.3.21 becomes

$$<B_n^+ B_n>=\frac{1}{e^{\frac{E_v}{k_B T}}-1},$$

(3.23)

while concentration of the pairs disappears. It means that realization requires annihilation of the pairs of elementary excitations.

4. Conclusion

Having in mind a series of protein activities, we decided to analyze possibility of metastable states of elementary excitations in proteins. The initial, stable Hamiltonian, cannot neither cover all activities of proteins nor explain different roles they play in physical processes.

So, we transformed initial stable Hamiltonian by means of unitary double coherent transformation and found equivalent metastable Hamiltonian which corresponds to reached set of processes. The most interesting process is forming of pairs and their decay. Besides, the elementary excitations in metastable states behave more „classically" than the elementary

excitations in stable states, since metastable poles are defined by $\omega^2 - \omega_{ex}^2 = 0$, i.e. analogously to quanta of mechanical vibrations and quanta of electromagnetic field (8).

This could open new directions in analyses of proteins and their role in physical processes.

Acknowledgements

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