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RELEVANCE OF POLARON/SOLITON-LIKE TRANSPORT IN CASCADE RESONANT ISOMERIC TRANSITIONS OF Q1D-MOLECULAR CHAINS

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ABSTRACT. Our recently proposed *quantum approach* to biomolecular *isomeric-conformational changes & recognition processes*, additionally *supported* by biomolecular *resonant recognition model* and quantum-chemical theory of *non-radiative resonant transitions*, is hereby *extended to cascade resonant transitions via close intermediate isomeric states* - which might be related to *polaron/soliton-like transport mechanisms in Q1D-molecular chains*, whose relevance is *explored* in this paper.

Keywords: ***Quantum Biophysics, Quantum Bioinformatics, Biomolecular Isomeric-Conformational Changes & Recognition, Non-Radiative Cascade Resonant Transitions, Q1D Polaron/ Soliton-like Transport Mechanisms.***

INTRODUCTION

Two unresolved issues of the (semi)classically addressed problems in *molecular biophysics* are *unreasonably* ***long time*** *necessary for change of biopolymer conformations* ***and*** *long-range* ***directivness*** *of selective biomolecular recognition processes* - implying their essential ***quantum nature*** [1].

Our previous results [1], describing general ***Quantum Decoherence*** framework for biopolymer conformational changes in very selective ligand-proteins/target-receptors key/lock biomolecular recognition processes, followed by electron-conformational coupling giving rise to ***dynamical modification*** of the many-electron energy-state hypersurface of the cellular quantum-ensemble ligand-proteins/target-receptors biomolecular macroscopic quantum system, revealed possibility to consider cellular biomolecular recognition as a ***Hopfield-like*** quantum-holographic associative neural network.

The quantum nature of these processes is additionally supported by the biomolecular ***Resonant Recognition Model*** (RRM) findings [2] that the *same characteristic single-electron RRM frequency*, and almost *opposite phase*, characterise biomolecular ligand-proteins and target-receptors *general function*, i.e. their biomolecular *recognition/interaction* (with numerous potential *practical advantages* for protein *de novo* design with *desired functions*). .

The quantum nature of biomolecular process can also be supported by quantum-chemical ***Theory of Non-Radiative Resonant Transitions*** in mono-molecular and bi-molecular reactions [3,4], realized through *intermediate quantum-coherent superpositions* of the externally perturbed electronic-vibrational states of the interacting biomolecules - revealing that the ***allowed transitions*** between isomeric states (*i,f*) are possible only for close states with ***nonvanishing*** *electronic and vibrational overlap integrals* S and S (cf. Fig. 1). This also applies to ***cascade*** *resonant transitions via* ***close intermediate*** *isomeric states* - which *might be related to* ***polaron/soliton-like*** *transport processes* through Q1D-(bio)molecular chains [5-11], that will be explored further on.

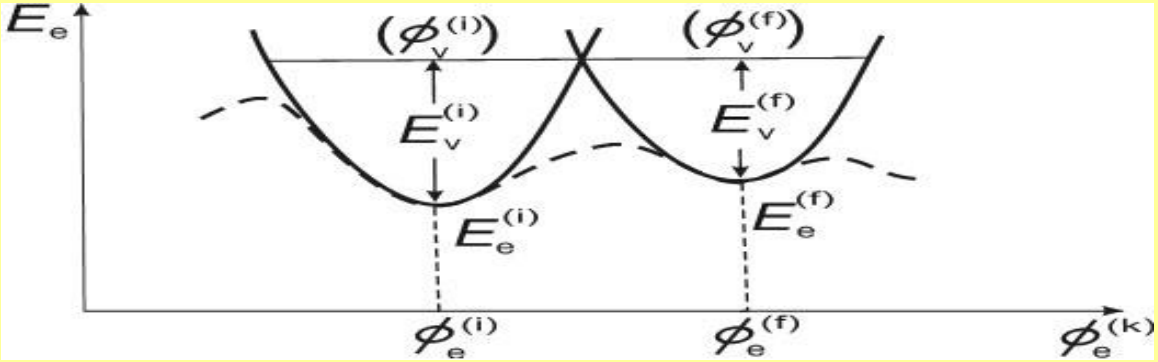


Figure 1. The (quasi)classical problem of ***many-electron hypersurface*** $E_e(\phi_e^{(k)})$, as a *potential energy* for adiabatically decoupled Q1D *vibrational* and *conformational system* (with local minima as semi-classical 'positions', i.e. many-atomic isomer configurations on many-electron hypersurface (*broken line* in the figure)) - not adiabatically well-defined when traversing between two adjacent local minima - is *replaced* in the ***Theory of Non-radiative Resonant Transitions*** by better defined problem of ***two (virtually intersecting) isomeric many-electron hypersurfaces*** (hyperparaboloids) serving as potential hypersurfaces for two *vibrational (isomeric) problems* (*full line* in the figure). In this approach, by ***external perturbation*** of the isomers, at this very intersection the conditions for ***electronic-vibrational non-radiative resonant transitions*** between the two isomers (*i, f*) are achieved: in the first approximation, the matrix element of ***dipole transition*** from *i*-th to *f*-th isomer is given by $\boldsymbol{\mu}^{(i,f)} \approx \boldsymbol{\mu}_e^{(i,f)} S_v^{(i,f)} + \boldsymbol{\mu}_v^{(i,f)} S_e^{(i,f)}$, so that ***allowed transitions*** between isomeric states (*i, f*) are possible only for ***close states*** *with nonvanishing* electronic and vibrational dipole moments, $\boldsymbol{\mu}_e^{(i,f)}$ and $\boldsymbol{\mu}_v^{(i,f)}$**,** *and* electronic and vibrational overlap integrals, $S_v^{(i,f)}$ i $S_e^{(i,f)}$, *or* in ***cascade resonant soliton-like transitions*** (cf. Fig.2) between *close intermediate participating isomeric states*! Also, during these resonant transitions the perturbed biomolecular system is shortly described by ***quantum-coherent superposition*** $(\phi_e^{(i)} \phi_v^{(i)} \pm \phi_e^{(f)} \phi_v^{(f)})/\sqrt{2}$, before its ***quantum decoherence*** into final electronic state $\phi_e^{(f)}$ or into initial electronic state $\phi_e^{(i)}$ (with subsequent deexcitations into lower vibrational states).

RELEVANCE OF POLARON/SOLITON-LIKE TRANSPORT MECHANISMS IN CASCADE RESONANT TRANSITIONS VIA CLOSE ISOMERIC STATES IN Q1D-MOLECULAR CHAINS

Various structural transformations of Q1D-molecular chains are characterized by *local rearrangements of atoms* between neighbor unit cells, with supposed significant role of ***low-frequency skeletal vibrations*** and their ***higher overtones***. Namely, neighbor atoms are approaching each other thus increasing probability for finding charged particles within chemical bonds, which might result in ***migrations of conjugated chemical bonds*** along Q1D-molecular chain as well as ***proton transfer*** from a carbon atom to its second neighbor, as it is the case for linear conjugated hydrocarbons.

However, a ***mechanism of directive transport of charged particles*** (electrons and protons) ***is sought for***, as *excited double CC bond* ***migrates gradually*** *along conjugated chain*, *which passes* ***through isomeric forms***. The mentioned explanation on atomic interactions *via* low-frequency skeletal vibrations seems to be incomplete, suggesting that the *chain is deformed in the presence of local excitation during its transport through conjugated chain*, and this very ***self-trapped autolocalized excitation*** (***polaron/soliton***) might be the *sought mechanism for directive* ***energy and charge transport*** *along Q1D-(bio)molecular chains*.

Theoretical basis for energy and charge transport phenomena in Q1D-molecular chains is the ***Frohlich Hamiltonian***:

$$H = \Delta\sum_n \hat{a}_n^{+}\hat{a}_n - J\sum_n \hat{a}_n^{+}(\hat{a}_{n+1} + \hat{a}_{n-1}) + \frac{1}{\sqrt{N}}\sum_{n,q} F_q e^{iqnR_0}\hat{a}_n^{+}\hat{a}_n(\hat{b}_q + \hat{b}_{-q}^{+}) + \sum_q \hbar\omega_q \hat{b}_q^{+}\hat{b}_q ,$$

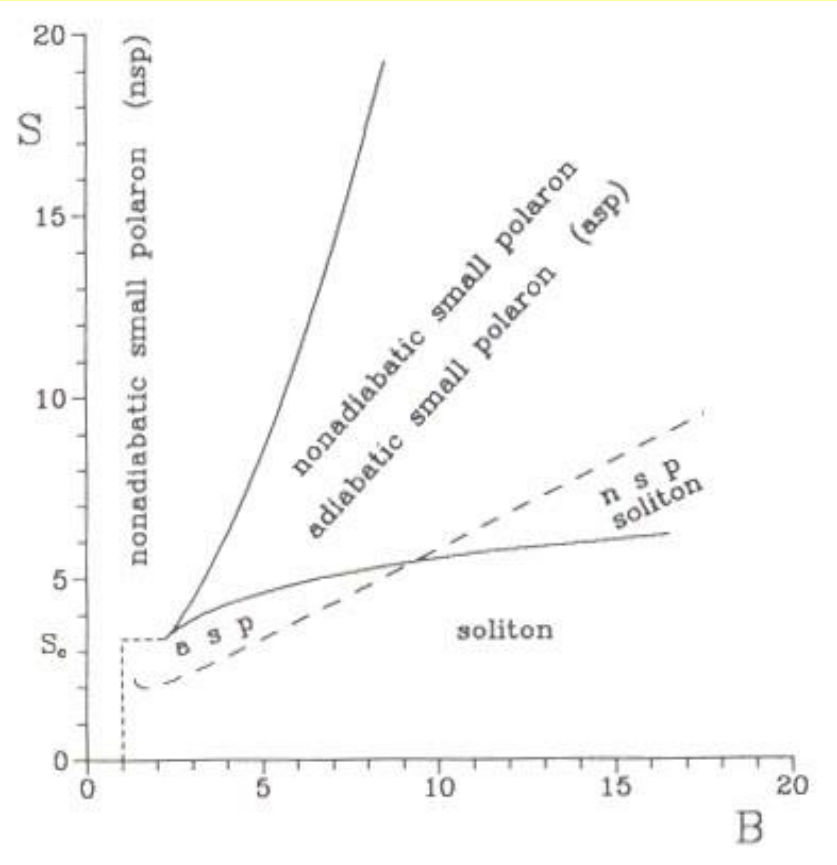
where Δ is the *molecular energy of exciton* (in general electron, vibron, hole…), $\hat{a}_n^{+}$ and $\hat{a}_n$ are creation and anihilation *exciton operators* on the *n*-th molecular lattice site respectively, *J* is the *energy of dipole-dipole coupling* of neighbor dipoles, $\hat{b}_q^{+}$ and $\hat{b}_q$ are creation and anihilation *phonon operators* of frequency ω_q respectively, $F_q = 2i\chi\left(\hbar/2M\omega_q\right)^{1/2} qR_0$ are *exciton-phonon coupling parameters*, while R_0 is *lattice constant*.

The above Hamiltonian in the *adiabatic region* leads to the ***wave function:***

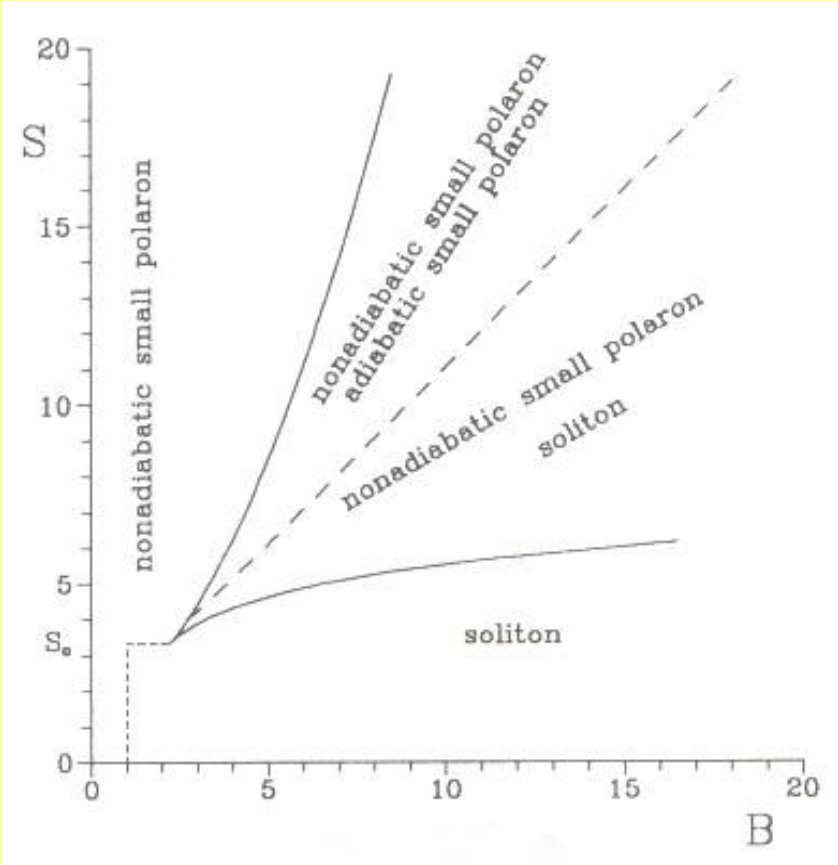
$$\phi(x,t) = \sqrt{\mu/2}\exp[i(k_s(x - x_0) - \omega_s t)]/\cosh[\mu(x - x_0 - \upsilon t)/R_0],$$

of the *exciton subsystem*: where μ represents *inverse width of the soliton*, $k_s = \hbar\upsilon/2JR_0^{\,2}$ is the *soliton quasi-momentum*, while ω_s is a *phase factor*.

Soliton, as non-linear excitation, propagates through the polymer chain in the form of an *entity created by* ***autolocalized exciton and lattice deformation***: $u(x,t) = u_0 \tanh[\mu(x - x_0 - \upsilon t)/R_0]$, where u_0 represents the *soliton amplitude* (width), which depends on the *exciton-phonon coupling strength* χ, the *chain elasticity constant k*, and the *soliton velocity* υ. The autolocalized exciton is 'dragging' the chain deformation, with enlarged *soliton effective mass*: $m_s^* = m_{ex}^*(1 + 3\pi^2 S^2/2)$ (holding true for exciton coupling with longitudinal acoustic phonons). The conditions for creation of soliton are fulfilled when its energy state is *lower* than energy of the free exciton (Δ): $E_s = \Delta - E_B{}^2/3J + m_s^* \upsilon^2/2$. The positive ***coupling constant*** $S \sim E_B/\hbar\omega_B$ (being S >> 1 for *adiabatic small polaron* concentrated on one site only, or S < 1 for *adiabatic large polaron–soliton* spread over the large number of lattice sites; where $E_B = \sum_q |F_q|^2/N\hbar\omega_q$ is the *binding energy of small polaron*) and ***adiabaticity parameter*** $B \sim E_{ex}/\hbar\omega_B$ (being B >> 1 in the *adiabatic limit*, when exciton energy $E_{ex} \sim 2J$ *largely exceeds* maximal phonon energy $\hbar\omega_B$, or covering other values in *nonadiabatic regime*) define the ***parametric space of autolocalized states*** which may lead, but not in all cases, to creation of solitons. The satisfactory description of ***classification and existence*** of autolocalized states in the parametric space of ***Q1D-materials*** was solved by *Ivić et al* and presented graphically in ***phase diagrams*** of Fig. 2.



(a)



(b)

Figure 2. The ***phase diagrams*** of *coupling constant* ($S \sim E_B / \hbar\omega_B$) *vs. adiabaticity parameter* ($B \sim E_{ex} / \hbar\omega_B$) in *Q1D exciton-phonon* system, for *exciton coupling* with: (a) *longitudinal acoustic phonons* (ADP-model), and (b) *optical phonons* (MCM-model).

MODEL ESTIMATIONS ON LINEAR CONJUGATED HYDROCARBONS

For *higher overtones of skeletal vibrations* ~ 1500 cm^{-1} [3] in *resonant isomer-isomer transitions* within *conjugated hydrocarbons chains*, the *maximal phonon energy* is $\hbar\omega_B$ ~ 0.15 eV. Then, taking into account that *interaction energy of accidental hopping* is proportional to the *electron (proton) band width* in double CC bond, $J \sim E_e$ ≥ (1.5 – 2) eV [11], one obtains for ***adiabaticity parameter***, $B \sim E_{ex}/\hbar\omega_B >> 1$.

Besides, for *slow polarons/solitons* the neglect of their dependence on the velocity enables the *following approximations*: $u_0 = \chi/k$, $E_B = \chi^2/k$ [10] (for *electron coupling with acoustic phonons*) i.e. $u_0 = \mu\chi/k$, $E_B = \chi^2/2M\omega_B{}^2$, $\mu = E_B/2J$ [10] (for *electron coupling with optical phonons*) - where χ is the *electron-phonon coupling strength*, *M* is the *mass of CH bond*, ω_B is *characteristic frequency of skeletal vibrations*, E_B is the *binding energy of small polaron*, and k is the *chain elasticity constant*. Then ***coupling constant***, $S \sim E_B/\hbar\omega_B$, for chosen values of parameters (χ = 4.1 eV/Å, k = 21 eV/$Å^2$ [11]) is S ≈ 5.33 for *exciton coupling with acoustic phonons*, i.e. S >> 1 for *exciton coupling with optical phonons*.

Then, on the basis of *phase diagrams* in parametric space of the autolocalized states (cf. Fig. 2), it can be concluded that *autolocalized states* in linear conjugated hydrocarbons have properties of ***adiabatic large polarons – solitons***.

Additionally, the polaron width on the basis of the above expressions is u_0 = 0.19 Å for ADP-model, i.e. $u_0 \approx$ (1.98 – 49) Å for MCM-model. So, as the length of CC bond is approximately R_0 ~ 1.5 Å, the width of large polaron is *nonrealistic* in the case of exciton coupling with acoustic phonons (ADP) - and it is reasonable to propose ***exciton coupling with optical phonons*** (MCM) during *isomeric transitions* in hydrocarbons conjugated chains, i.e. *optical phonons* can have major role in *skeletal hydrocarbons conjugated chain deformations*.

These estimations are *in accordance* with *theoretical predictions* of the ***solitons*** in ***trans-polyacetilene*** [11], and presence of the *anomalous line in its infrared spectrum* [12-14] as one of the most convincing evidences for their existence: on the basis of explanation of Scott *et al* [12] the *missing intensity of this infrared line* originates from the *scattering on solitons*, produced by *coupling of intramolecular excitation with in-plane C-H bending vinylene phonon mode*. As in trans-polyacetilene the width of electronic band is 0.64 eV and maximal phonon energy is 0.06 eV (and correspondingly 2.5 eV and 1.6 eV in polydiacetilene) [15] - for these values one obtains $B \geq 1$, which satisfies two basic conditions (adiabatic and continuum approximation [9]) that ***electron autolocalization*** can lead to creation of ***adiabatic large polarons – solitons*** in these extended hydrocarbon conjugated polymers [9]. Finally, on the basis of above parameters it is also possible to estimate the *soliton radius* in the range of 5 – 10 unit lengths (while effective polaron mass varies from ~ m_0 (electron mass) for trans-polyacetilene to ~ 100 m_0 for polydiacetilene).

It should be also added, that ***vibron autolocalization*** in extended hydrocarbon conjugated trans-polyacetilene can lead to creation of ***nonadiabatic small polarons***, as predicted by Alexander and Krumhansl [16].

CONCLUSION

Quantum approach to biomolecular ***isomeric-conformational changes***, *previously developed* in the framework of *quantum-chemical theory* of biomolecular ***non-radiative resonant transitions*** and *further extended* to ***cascade resonant transitions*** *via* ***close intermediate isomeric states*** - is *hereby theoretically explored* in the framework of ***phase diagrams*** *of* ***polaron/soliton-like transport processes*** *in* ***Q1D-(bio)molecular chains*** - of potential importance for quantum biophysics and quantum bioinformatics, nanobiology and nanotechnology.

Our *model estimations* on the *hydrocarbon conjugated chains* reveal that ***autolocalization of charged particles*** in them can lead to creation of ***adiabatic large polarons - solitons***, while ***optical phonons*** of the conjugated chains can have *major role in skeletal chain deformations* during ***soliton-like cascade resonant transitions*** *via* ***close intermediate isomeric states***.

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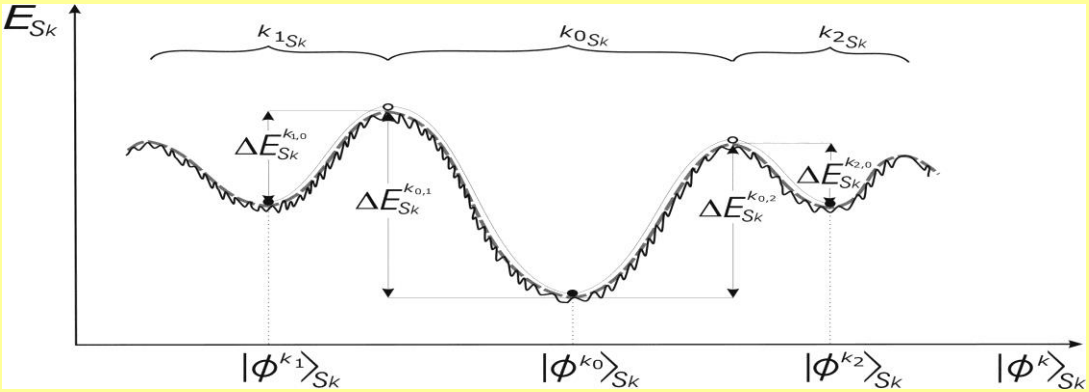

Figure 3. Schematic presentation of memory attractors in energy-state hypersurface ($E_{S_k}(\phi^{k_i})$) of ***quantum-holographic memory/propagator cellular quantum-ensemble ligand-proteins/target-receptors biomolecular macroscopic open quantum system***: $G^{(k)}(\boldsymbol{r_2},t_2,\boldsymbol{r_1},t_1) = \sum_{i=0}^{P_k-1} \phi^{(k_i)}(\boldsymbol{r_2},t_2)\,\phi^{(k_i)}(\boldsymbol{r_1},t_1)^* = \sum_{i=0}^{P_k-1} A_{k_i}(\boldsymbol{r_2},t_2)\,A_{k_i}(\boldsymbol{r_1},t_1)\; e^{\frac{i}{\hbar}(\alpha_{k_i}(r_2,t_2)-\alpha_{k_i}(r_1,t_1))}$ – and the same holds true for higher quantum-holographic hierarchical level of ***acupuncture system/consciousness***! It should be pointed out that ***quantum decoherence*** evidently plays ***fundamental role*** *in biological quantum-holographic neural networks*, through presented ***shape adaptation of energy-state hypersurface*** (in contrast to *artificial qubit quantum computers* where quantum decoherence must be *avoided* until the final read-out act of quantum computation) – which implies that Nature has chosen elegant ***room-temperature solution*** for ***biological quantum-holographic information processing***, continuously ***fluctuating*** *between* ***quantum-coherent state*** $\left|\phi^k(t)\right\rangle_{S_k} = \sum_i c_{k_i}(t)\left|\phi^{k_i}\right\rangle_{S_k}$ *and* ***classically reduced state*** $\hat{\rho}^k_{S_k}(t) = \sum_i \left|c_{k_i}(t)\right|^2 \left|\phi^{k_i}\right\rangle_{S_kS_k}\left\langle\phi^{k_i}\right|$ of *acupuncture system/ consciousness*, through nonstationary interactions with out-of-body far-environment and through decoherence by body near-environment. Hence, ***quantum neural holography*** combined with ***quantum decoherence*** might be very significant element of feed-back ***bioinformatics***, *from the level of cell to the level of organism*!