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

G. Keković¹, D. Raković¹, D. Davidović²,³

¹ Faculty of Electrical Engineering, Belgrade, Serbia
² Vinca Institute of Nuclear Sciences, Belgrade, Serbia
³ School of Electrical and Computer Engineering, RMIT, Melbourne, Australia
**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 $E_{e}(\phi^{(k)}_{e})$, 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 $\mu^{(i,f)} \approx \mu^{(i,f)}_{e} S^{(i,f)}_{v} + \mu^{(i,f)}_{v} S^{(i,f)}_{e}$, so that allowed transitions between isomeric states ($i, f$) are possible only for close states with nonvanishing electronic and vibrational dipole moments, $\mu^{(i,f)}_{e}$ and $\mu^{(i,f)}_{v}$, and electronic and vibrational overlap integrals, $S^{(i,f)}_{v}$ i $S^{(i,f)}_{e}$, 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 $(\phi^{(i)}_{e} \pm \phi^{(f)}_{e})/\sqrt{2}$, before its quantum decoherence into final electronic state $\phi^{(f)}_{e}$ or into initial electronic state $\phi^{(i)}_{e}$ (with subsequent deexcitations into lower vibrational states).
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:

\[
H = \Delta \sum_n \hat{a}_n^+ \hat{a}_n - J \sum_n \hat{a}_n^+ (\hat{a}_{n+1} + \hat{a}_{n-1}) + \frac{1}{\sqrt{N}} \sum_{n,q} F_q e^{i q R_0} \hat{a}_n^+ \hat{a}_n (\hat{b}_q + \hat{b}_{-q}^+) + \sum_q \hbar \omega_q \hat{b}_q^+ \hat{b}_q,
\]

where \(\Delta\) 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 \(\omega_q\) respectively, \(F_q = 2i \chi (\hbar/2M \omega_q)^{1/2} q R_0\) are exciton-phonon coupling parameters, while \(R_0\) is lattice constant.

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

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

of the exciton subsystem: where \(\mu\) represents inverse width of the soliton, \(k_s = \hbar \nu / 2JR_0^2\) is the soliton quasi-momentum, while \(\omega_s\) 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**: 

\[ u(x,t) = u_0 \tanh[\mu(x-x_0-\nu t)/R_0], \]

where \( u_0 \) represents the **soliton amplitude** (width), which depends on the **exciton-phonon coupling strength** \( \chi \), the **chain elasticity constant** \( k \), and the **soliton velocity** \( \nu \). 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 (\( \Delta \)): 

\[ E_s = \Delta - E_B^2 / 3J + m_s^* \nu^2 / 2. \]

The positive **coupling constant** \( S \sim E_B / \hbar \omega_B \) (being \( S \gg 1 \) 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 \( B \gg 1 \) 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.
Figure 2. The **phase diagrams** of coupling constant \( S \sim \frac{E_B}{\hbar \omega_B} \) vs. adiabaticity parameter \( B \sim \frac{E_{ex}}{\hbar \omega_B} \) in Q1D exciton-phonon system, for exciton coupling with: (a) **longitudinal acoustic phonons** (ADP-model), and (b) **optical phonons** (MCM-model).
MODEL ESTIMATIONS ON
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For higher overtones of skeletal vibrations $\sim 1500$ cm$^{-1}$ [3] in resonant isomer-isomer transitions within conjugated hydrocarbons chains, the maximal phonon energy is $\hbar \omega_B \sim 0.15$ eV. Then, taking into account that interaction energy of accidental hopping is proportional to the electron (proton) band width in double CC bond, $J \sim E_e \geq (1.5 - 2)$ 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 $\chi$ is the electron-phonon coupling strength, $M$ is the mass of CH bond, $\omega_B$ 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 ($\chi = 4.1$ eV/Å, $k = 21$ eV/Å$^2$ [11]) is $S \approx 5.33$ 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 $u_0 = 0.19 \, \text{Å}$ for ADP-model, i.e. $u_0 \approx (1.98 - 49) \, \text{Å}$ for MCM-model. So, as the length of CC bond is approximately $R_0 \sim 1.5 \, \text{Å}$, 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-polyacetylene [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-polyacetylene 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 polydiacetylene) [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 $\sim m_0$ (electron mass) for trans-polyacetylene to $\sim 100 m_0$ for polydiacetylene).

It should be also added, that vibron autolocalization in extended hydrocarbon conjugated trans-polyacetylene 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.
REFERENCES


Figure 3. Schematic presentation of memory attractors in energy-state hypersurface \((E_{Sk} (\phi^k))\) of quantum-holographic memory/propagator cellular quantum-ensemble ligand-proteins/target-receptors biomolecular macroscopic open quantum system: \(G^{(k)}(r_2,t_2,r_1,t_1) = \sum_{i=0}^{P_k-1} \phi^{(k_i)}(r_2,t_2) \phi^{(k_i)}(r_1,t_1)^* = \sum_{i=0}^{P_k-1} A_{k_i} (r_2,t_2) A_{k_i} (r_1,t_1) e^{i\hbar (\alpha_{k_i}(r_2,t_2) - \alpha_{k_i}(r_1,t_1))}\). – 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-coherence 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 \(\tilde{\rho}^k_{S_k}(t) = \sum_i |c_{k_i}(t)|^2 \left| \phi^k_i \right\rangle_{S_k} \langle \phi^k_i |\) 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 feedback bioinformatics, from the level of cell to the level of organism!