Relevance of Polaron/Soliton-Like Transport Mechanisms in Cascade Resonant Isomeric Transitions of Q1D-Molecular Chains

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

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 *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, characterize biomolecular ligand-proteins and target-receptors general function, i.e. their biomolecular recognition/interaction (with numerous potentially practical advantages for protein *de novo* design with desired functions in the fields of molecular biology, biotechnology, medicine, agriculture and nanotechnology).

On the other hand, 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 $S_e^{(i,f)}$ and $S_v^{(i,f)}$ (cf. Fig. 1). This also applies to *cascade* resonant transitions via *close intermediate* participating 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.
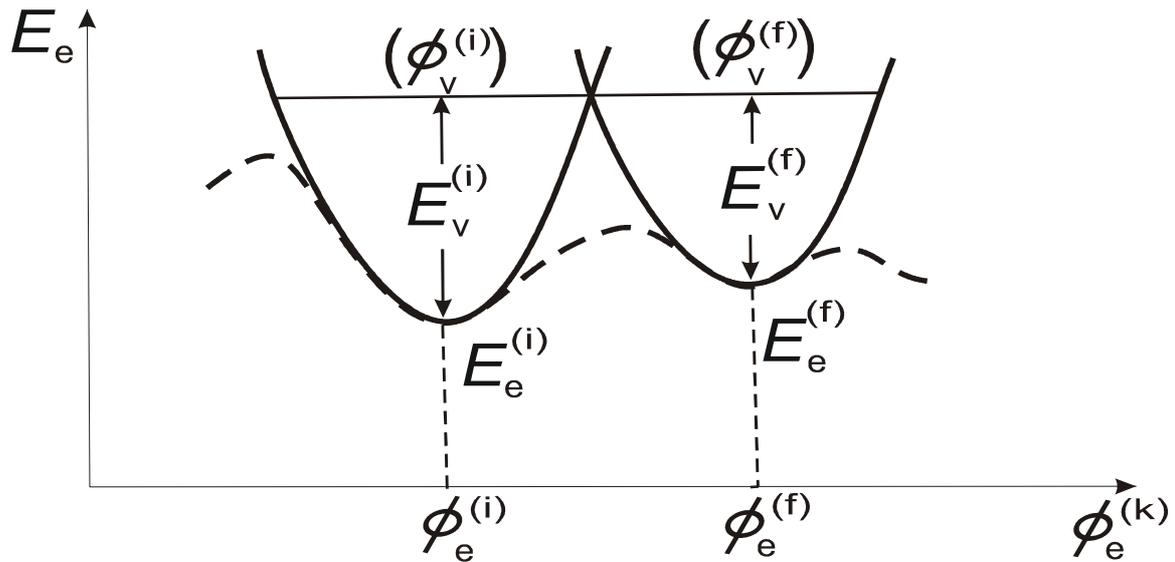
Fig. 1 The (quasi)classical problem of *many-electron hypersurface* $E_e(\phi^{(k)})$ as *potential energy* for adiabatically decoupled quasi-one-dimensional *vibrational* and *conformational system* (with local minima as semi-classical 'positions', i.e. many-atomic isomer configurations on many-electron hypersurface (*broken line* in the figure)) - not adiabatically well-defined when traversing between two adjacent local minima - is *replaced* in the framework of 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) [3,4]. 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 $\boldsymbol{\mu}^{(i,f)} \approx \boldsymbol{\mu}_e^{(i,f)} S_v^{(i,f)} + \boldsymbol{\mu}_v^{(i,f)} S_e^{(i,f)}$, and it is obvious that transition between two isomers will be allowed when components of corresponding electronic and vibrational dipole moments, $\boldsymbol{\mu}_e^{(i,f)}$ and $\boldsymbol{\mu}_v^{(i,f)}$, *and* electronic and vibrational overlap integrals, $S_v^{(i,f)}$ and $S_e^{(i,f)}$, *do not vanish*! 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 Intermediate 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 [3]. Namely, neighbor atoms are approaching each other thus increasing the probability density 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 [3]. However, a mechanism of directive transport of charged particles (electrons and protons) is sought, as excited double CC bond migrates gradually along conjugated chain, which passes through corresponding isomeric forms. The mentioned explanation of 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 [5-11].

Theoretical basis for energy and charge transport phenomena in Q1D-molecular chains is the Frohlich Hamiltonian, most frequently presented in the form [5]:

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

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, $F_q = 2i\chi(\hbar/2M\omega_q)^{1/2}qR_0$ are exciton-phonon coupling parameters, while R_0 is the lattice constant.

Mathematical analysis of the above Hamiltonian in adiabatic region is applied by using variational method [6], and results in the wave function of the exciton subsystem: $\phi(x,t) = \sqrt{\mu/2} \exp[i(k_s(x-x_0) - \omega_s t)]/\cosh[\mu(x-x_0-\upsilon t)/R_0]$, where μ represents inverse width of the soliton, $k_s = \hbar\upsilon/2JR_0^2$ is the soliton quasi-momentum, while ω_s is an irrelevant 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 described by expression: $u(x,t) = u_0 \tanh[\mu(x-x_0-\upsilon t)/R_0]$, where u_0 represents the soliton amplitude (width), which depends on the exciton-phonon coupling strength χ, chain elasticity constant *k*, and the soliton velocity υ. The autolocalized exciton is 'dragging' the chain deformation, giving rise to enlarged *effective mass* of soliton compared to the exciton: $m_s^* = m_{ex}^*(1 + 3\pi^2 S^2/2)$ (this expression holding true for the case of exciton coupling with longitudinal acoustic phonons). The conditions for the creation of soliton are fulfilled when its energy state is lower than the energy of the free exciton (Δ): $E_s = \Delta - E_B^2/3J + m_s^*\upsilon^2/2$.

The positive definite *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 the creation of solitons: The satisfactory description of *classification and existence* of autolocalized states in the parametric space of Q1D-molecular chains was successfully solved in several papers of Ivić *et al.* [8-10] and presented graphically in the *phase diagrams* of Fig. 2 [9], for the cases of *exciton coupling with longitudinal acoustic phonons* (ADP-model, Fig. 2a) and *exciton coupling with optical phonons* (MCM-model, Fig. 2b), respectively. On the basis of these results, it is possible to explore the *relevance* of the polaron/soliton mechanisms in energy and charge transport phenomena within various Q1D-materials: it is only necessary to calculate S and B parameters for them, and afterwards to find their points in the parametric space of Fig. 2.
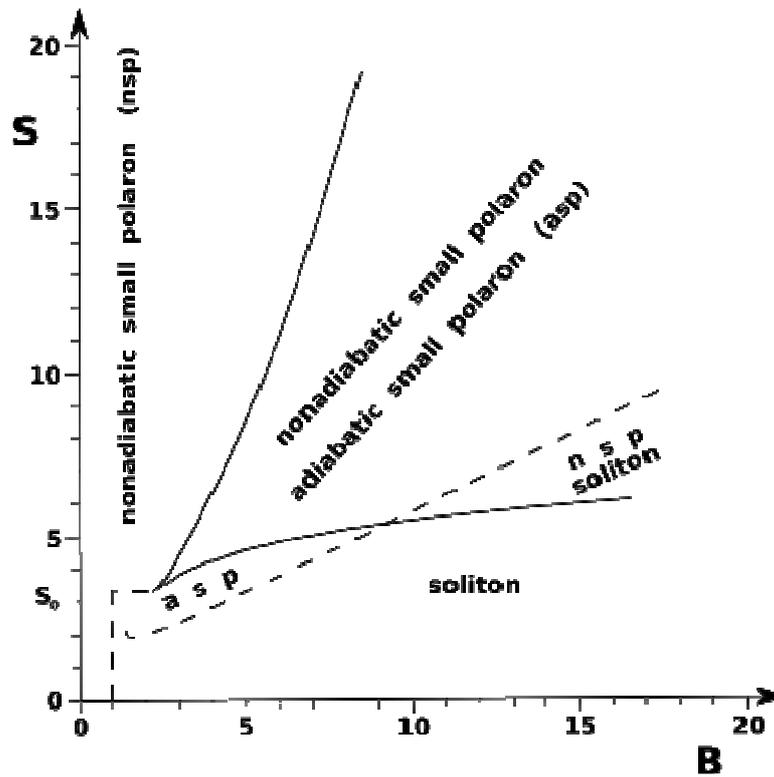
(a)
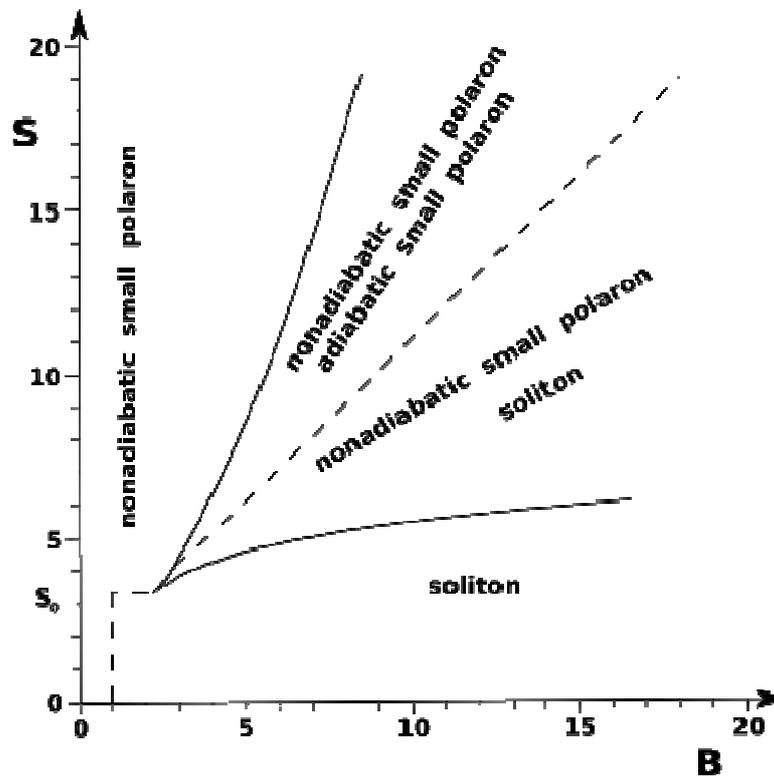
(b)

Fig. 2 The phase diagrams of Q1D exciton-phonon system, for exciton coupling with: (a) longitudinal acoustic phonons (ADP-model), and (b) optical phonons (MCM-model); adapted from [9].

Further on, we shall estimate the corresponding values in parametric space of autolocalized states for linear conjugated hydrocarbons, whose higher overtones of skeletal vibrations in resonant

isomer-isomer transitions within conjugated hydrocarbons chains are ~ 1500 cm^{-1} [3], i.e. 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 $B >> 1$. Besides, we shall consider the case of slow polarons/solitons, i.e. we shall neglect their dependence on the velocity, which enables the following approximations: $u_0 = \chi/k$, $E_B = \chi^2/k$ [10] for the case of 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 the case of electron coupling with optical phonons (χ is the electron-phonon coupling strength, M is the mass of CH bond, ω_B is the characteristic frequency of skeletal vibrations, E_B is the binding energy of small polaron, and k is the chain elasticity constant). The 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 the case of exciton coupling with acoustic phonons, i.e. $S >> 1$ for the case of exciton coupling with optical phonons. On the other hand, 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. Then, on the basis of 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, as the length of CC bond is approximately $R_0 \sim 1.5$ Å, the width of large polaron is nonrealistic in the case of exciton coupling with acoustic phonons (ADP) - so 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 chain deformations.

These estimations are in accordance with theoretical predictions of the *solitons* in trans-polyacetilene [11], and the 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 the 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-polyacetilene to ~ 100 m_0 for polydiacetilene).

It should be also added, that *vibron autolocalization* in extended hydrocarbon conjugated trans-polyacetilene can lead to the 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 participating 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 the 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 participating isomeric states.

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